THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVI SEPTEMBER 1951 No. 9

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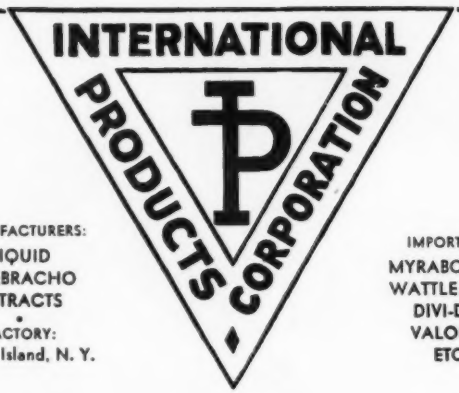

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B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

Ask about Mead Cold Soluble Chestnut Extract for retanned leathers. And—for more pounds of plumper leather—standardize on Mead Chestnut Extract.

IT'S A FACT!

Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

Vegetable Tannin	Tan Yard Yield (*white weight basis*)
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

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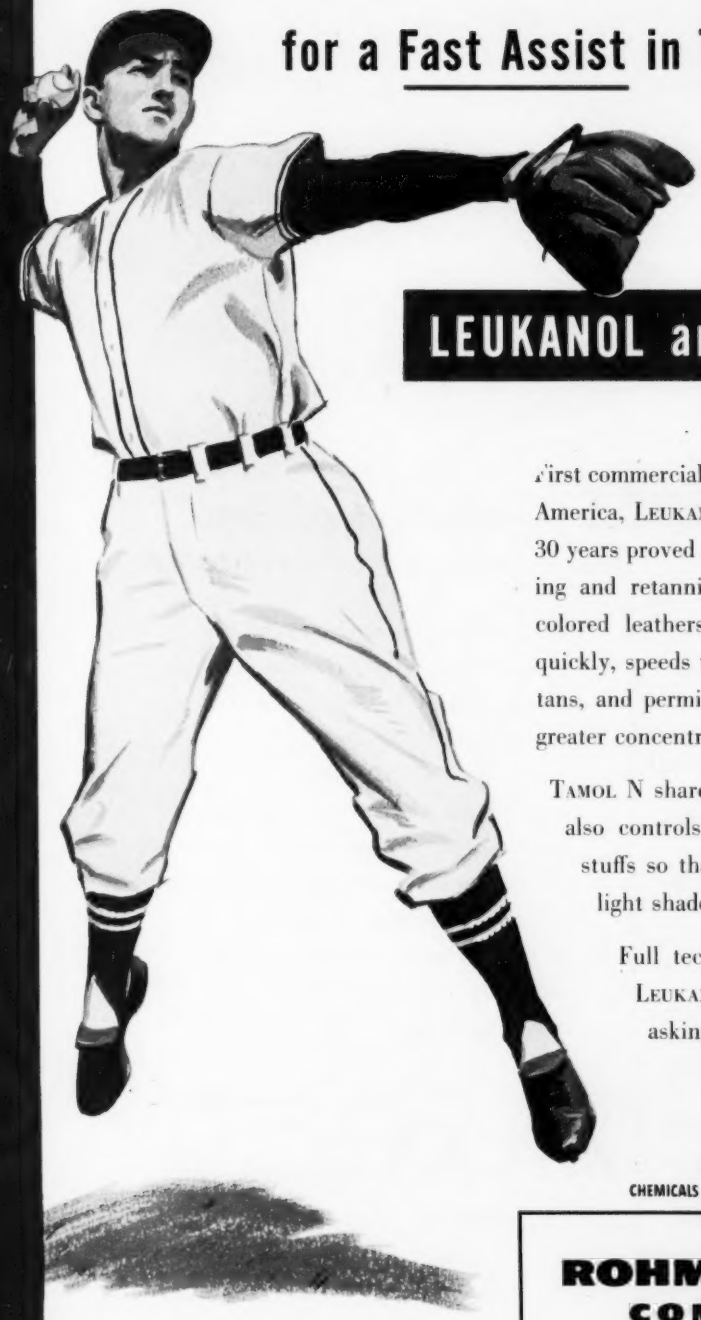

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M.P. . . . . 100°C

Light buff colored solid in flake form. Rapidly soluble in water; slightly soluble in alcohol; insoluble in ether. Also available in solid form.

ANALYSIS

Na_2S	60 to 62%
NaCl	1.5% Max.
Other Na Salts	2.0% Max.
Fe	8 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	35% Min.

SHIPPING CONTAINERS

Steel drums . . . . 90 and 350 lbs. net

SODIUM SULFHYDRATE—NaSH

(sodium hydrosulfide)

Mol. Wt. 56.1
M.P. . . . . 55°C

Light lemon colored solid in flake form. Completely and rapidly soluble in water, alcohol and ether.

ANALYSIS

NaSH	70 to 72%
Na_2S	2.5% Max.
NaCl	0.8% Max.
Na_2SO_3 and $NaHCO_3$	0.4% Max.
Fe	5 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	28 to 26%

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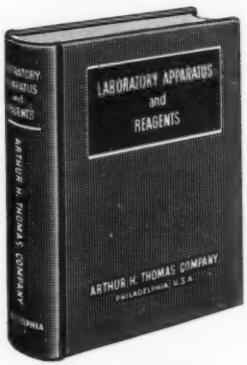

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JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVI SEPTEMBER 1951 No. 9

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SECRETARY'S NOTICE

It has been approved by the Association that beginning January 1952, the annual dues will be $12.00 per year. Mutual Membership will be $17.00 per year.

Beginning January 1952, all subscriptions to the Journal will be $15.00 per year, with a charge of $1.50 for postage on all subscriptions outside the continental limits of the United Sates, excepting Canada.

Single issues of the Journal will remain at $2.00 per copy.

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Wanted: Color Matcher and Finish Compounder by Manufacturer of Tannery Finishes for laboratory development work. This position requires a complete knowledge of the use of dyes and pigments as applied to the leather finish field, and the ability to use that knowledge to maximum effect in compounding with our complete line of pigment binders, etc. Will work directly with Laboratory Director in modern air-conditioned laboratory, completely equipped to finish all types of leather, from spray application thru plating or glazing operations. Please give complete resume of past experience and qualifications along with personal data and salary desired. Please address your reply to—Box HB-514, Dr. Fred O'Flaherty, Dept. of Tanning Research, University of Cincinnati, Cincinnati 21, Ohio.

Leather Chemist: 35 years of age, thoroughly experienced in the manufacturing of bark and chrome tanned shoe and fancy leathers from beaming to finishing. Capable of managing and supervising plant production. Is looking for adequate position. Please address your reply to—Box CI-201, Dr. Fred O'Flaherty, Dept. of Tanning Research, University of Cincinnati, Cincinnati 21, Ohio.

Wanted: Assistant to Tannery Superintendent:

Man-age 26 to 36-with tannery experience. Preferably one educated at Pratt Institute or the University of Cincinnati tannery schools. Requirements: knowledge of chemistry, tannery operation, supervision and management of men, routine tannery office clerical duties. Position offers interesting opportunity for advancement. Please write all details and address your reply to—EFH-303, Dr. Fred O'Flaherty, Dept. of Tanning Research, University of Cincinnati, Cincinnati 21, Ohio.

Association Membership and Journal Circulation Report

Status of Association
as of February 1, 1951

MEMBERS:			
Active	418	New in 1950	67
Associate	356	Lost in 1950	59
Student	15		
	789	Gain	8
SUBSCRIBERS:			
Domestic	110	New in 1950	111
Foreign	183	Lost in 1950	48
	293	Gain	63
MUTUAL MEMBERS (S.L.T.C.)	162	Increase Over 1950	15
EXCHANGE SUBSCRIPTIONS:			
Domestic	12		
Foreign	38	Increase over 1950	4
Canadian	2		
	52		
COPIES TO ADVERTISERS:	94	Gained in 1950	3
TOTAL JOURNAL CIRCULATION	1390	Increase over 1950	93

Circulation Breakdown

	United States	Foreign	Canadian	Total
Active Members	362	29	27	418
Associate Members	299	35	22	356
Student Members	15			15
Mutual Members		162		162
Subscribers	101	183	9	293
Exchange	12	38	2	52
Advertisers	94			94
	883	447	60	1390

Members Breakdown

	Active	Associate	Student	Total
Maine	2	0	0	2
New Hampshire	4	5	0	9
Vermont	0	0	0	0
Massachusetts	44	53	3	100
Rhode Island	0	2	0	2
Connecticut	2	3	0	5
New York	59	49	10	118

New Jersey	45	44	0	89
Pennsylvania	61	45	0	106
Delaware	10	10	0	20
Maryland	6	7	0	13
Washington, D. C.	4	0	0	4
Virginia	11	2	0	13
West Virginia	2	2	0	4
North Carolina	3	2	0	5
South Carolina	0	0	0	0
Georgia	3	2	0	5
Florida	0	1	0	1
Kentucky	1	0	0	1
Tennessee	6	2	0	8
Alabama	0	0	0	0
Mississippi	0	0	0	0
Ohio	18	9	0	27
Indiana	1	1	0	2
Illinois	24	26	0	50
Michigan	9	2	0	11
Wisconsin	32	19	1	52
Minnesota	3	0	1	4
Iowa	0	2	0	2
Missouri	8	6	0	14
North Dakota	0	0	0	0
South Dakota	0	0	0	0
Nebraska	0	0	0	0
Arkansas	0	0	0	0
Louisiana	0	0	0	0
Oklahoma	0	0	0	0
Texas	0	1	0	1
Montana	0	0	0	0
Idaho	0	0	0	0
Wyoming	0	0	0	0
Colorado	0	0	0	0
New Mexico	0	0	0	0
Arizona	0	0	0	0
Utah	0	0	0	0
Nevada	0	0	0	0
Washington	0	0	0	0
Oregon	0	0	0	0
California	4	4	0	8
	362	299	15	676

Members Breakdown

	Active	Associate	Student	Total
United States	362	299	15	676
Canada	27	22		49
Foreign	29	35		64
	418	356	15	789

Foreign Members Breakdown

	Active	Associate	Total
Israel	1	0	1
India	3	1	4
Cuba	2	2	4
Belgium	0	3	3
Brazil	4	3	7
South Africa	1	1	2
Switzerland	2	0	2
France	2	2	4
Norway	0	1	1
Italy	1	1	2
Argentina	3	3	6
Mexico	1	2	3
Greece	1	1	2
England	1	1	2
Germany	1	1	2
Rhodesia	1	0	1
Philippines	2	0	2
Australia	0	1	1
Peru	0	3	3
Paraguay	0	1	1
Sweden	2	2	4
Uruguay	0	1	1
Chile	0	2	2
New Zealand	0	2	2
Spain	0	1	1
Norway	1	0	1
	29	35	64

Exchange List Breakdown

United States	Foreign	Canadian	Total
12	38	2	52

Advertisers — Free Copies

United States	94

S.L.T.C. Mutual Members Breakdown

England	99	Belgium	1
Australia	31	Portugal	1
New Zealand	3	Argentina	1
Sweden	2	Erie	1
Ireland	5	Peru	1
Scotland	5	Pakistan	1
Wales	1	India	2
South Africa	6	Greece	1
		Egypt	1

Foreign Subscribers Breakdown

Australia	19	Chile	2
Italy	9	Siam	1
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Portugal	4	Spain	3
Germany	10	Scotland	1
Russia	11	Japan	16
Switzerland	5	Turkey	1
Belgium	4	Roumania	2
Sweden	6	Indonesia	2
Holland	10	Finland	6
Norway	6	Yugoslavia	3
Hungary	4	Czechoslovakia	3
Mexico	6	Pakistan	2
South Africa	3	Peru	1
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Formosa	1	Austria	1
Denmark	3		
Brazil	7		183

United States Subscribers Breakdown

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Delaware	5	Oregon	1
Connecticut	3	Louisiana	1
Massachusetts	8	Missouri	3
Illinois	6	Washington, D. C.	2
Minnesota	2	Wisconsin	2
Pennsylvania	9	Washington	1
Maryland	2	Alabama	1
New Jersey	6	Tennessee	1
California	7	Florida	1
Ohio	4	Kentucky	1
Michigan	4	Canada	9
Georgia	1		
Iowa	1		100
North Carolina	1		
Texas	2		

MINUTES OF THE PHYSICAL TESTING COMMITTEE MEETING HELD AT THE HOTEL GRISWOLD, GROTON, CONNECTICUT June 10, 1951

The following members were present:

J. H. Gregory—Sears Roebuck & Company
J. W. Harnly—A. H. Ross & Sons, Company
R. B. Hobbs—National Bureau of Standards.
A. N. Kay—Howes Leather Company, Inc.

R. M. Lollar—University of Cincinnati.
C. W. Mann—Office of the Quartermaster General.
F. F. Marshall—Keystone Tanning and Glue Company.
C. P. McKee—International Shoe Company.
E. G. Railo—United States Testing Company.
W. T. Roddy—University of Cincinnati.
J. S. Rogers—Eastern Regional Research Laboratories.
Robert Shaw—Rohm & Haas Company.
E. B. Thorstensen—S. B. Foot Tanning Company.
Guests:
N. C. Benrud—S. B. Foot Tanning Company.
I. D. Clarke—Eastern Regional Research Laboratories.
Robert Hague—Rhoads Leather Company.
J. R. Kanagy—National Bureau of Standards.
R. H. Koehrmann—International Shoe Company.
W. M. Parker—Griess & Fleger Tanning Company.
C. G. Telander—Armour Leather Company.
J. F. Wagoner—Armour Leather Company.

Report of the Federal Specifications Board—American Leather Chemists Association Committee on Methods' Revision

Mr. E. B. Thorstensen reported that the Joint Committee completed its work in November, 1950. On December 19, 1950, Mr. Thorstensen, acting as chairman of the committee, transmitted the final report to M. Maeser, chairman of the Physical Testing Committee. This report contained a number of final corrections which were to be made on the proposed Federal Specifications KK-L-311, groups 2,000, 3,000 and 4,000. The proposed changes were accepted unanimously by the Joint Committee except for one objection by Mr. J. H. Gregory. This objection was relative to the necessity of purchasing new dies with which to cut certain test specimens. The changes transmitted to the American Leather Chemists Association by Mr. Thorstensen were transmitted to the Joint Committee by the Federal Specifications Board. The Federal Specifications Board has been in the process of incorporating these changes in new proposed revisions of the methods. Dr. Robert Hobbs of the National Bureau of Standards reported that the new revisions are nearly ready for reprinting. As soon as the new printing has been made, copies of the methods will be secured for an American Leather Chemists Association editorial subcommittee which will revise and reword the methods into a form more suitable for the purposes of the American Leather Chemists Association. It could not be determined just how soon the proposed revisions would be available for subcommittee action.

Fire Resistance of Leather

The Fire Resistance Subcommittee of which Mr. R. M. Lollar is chairman submitted its report to the Physical Testing Committee at the annual meeting in 1950. A suggested Fire Resistance Method was also submitted at that time. This method was circulated among the members of the committee and certain suggestions regarding its revision were made. These changes and corrections have been made by Mr. Lollar and the method has been resubmitted for action. The new method will be sent to the members of the committee for any additional corrections or changes which should be made. After the comments of the members of the committee have been received, the method will be turned over to the editorial subcommittee to be written up for submission to the Council as a tentative method of the Society.

Deterioration of Upper Leather Due to Perspiration

The attention of the chairman of the Physical Testing Committee has been called to the fact that the upper leather in a small number of shoes deteriorates very rapidly, due, apparently, to the perspiration from the foot soaking through the leather causing a hardening and embrittlement in the vamp section of the shoe. The advisability of our committee attempting to develop a method for determining the resistance of upper leather to deterioration by perspiration or a combination of perspiration and flexing was discussed. The committee felt that inasmuch as the National Bureau of Standards and the Office of the Quartermaster General Laboratory at Philadelphia were working on deterioration of upper leather, it would be best to take no action until these laboratories had obtained some concrete data which could be used to give a clearer picture of what might be involved in such a study.

Accelerated Aging

In 1944 the Association adopted an accelerated aging test in which leather was heated in a controlled atmosphere at 100°C. for a period of time. The decrease in tensile strength was determined and used as a measure of the deterioration of the leather. The method was dropped by the Association in 1948. The upholstery leather manufacturers have developed their own method for accelerated aging. This method consists of storing leather in a controlled atmosphere at 158°C. for a given period of time and determining the loss in tensile strength. The committee feels that such a method has no proven relationship to accelerated aging and any such method should be entitled "Temperature Deterioration of Leather". Mr. W. T. Roddy of the Tanners' Council Research Laboratory has agreed to look up some work which has been done to show the effect of storing leather at high temperatures to see if enough effect is produced by such storage to justify the development of a method for measuring this effect.

Simplification of Test Methods

If the proposed revision of the American Leather Chemists Association—Federal Specifications Board Joint Committee goes into effect, the Society will have eight methods for determining strength properties of leather. These include tensile strength, breaking strength, tearing strength by five methods, tongue, split, buckle, stitch with a single hole and stitch with a double hole, and bursting strength. There is a very strong feeling among a number of people in the industry that these tests all measure different aspects of the same property of leather and are, therefore, not necessary. Dr. Roddy and Dr. J. R. Kanagy of the National Bureau of Standards have agreed to go over data which is available and see if there is enough relationship between the results obtained by these various methods that part of the methods could be safely eliminated.

Numbering of the Society's Methods

Several members of the Association have suggested that the methods of the Association should be numbered in a more consistent manner. This includes physical testing, chemical and all other methods of the Association. It has been suggested by these members that a numbering system which could be consistently used for all the Association's methods be adopted. The Physical Testing Committee recommends that Council give consideration to the appointment of a special committee to consider this problem.

M. Maeser, Chairman
Physical Testing Committee

Extensibility of Hydrated Collagen

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University of California School of Medicine,
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INTRODUCTION

Individual collagen fibrils can be considerably lengthened by stretching. This may be witnessed in the electron microscope when the physical changes that occur in the supporting paralodion film and/or metallic grid manifest themselves in a stretching of the overlying tissue. The elongation that the constituent axial periods undergo as a result of these changes may culminate in rupture of the fibril. The maximum reported elongation occurring under these circumstances in teased and air-dried collagen is 5800A°. However,

*Damon Runyon Clinical Research Fellow of the American Cancer Society, as recommended by the Committee on Growth of the National Research Council.

This investigation was supported by the Institutional Grant of the American Cancer Society to the University of California School of Medicine.

when this method of stretching is used, the maximum obtainable increment compatible with the integrity of the fibril cannot be measured directly on electron micrographs. In fact, because of the continuous action of the elongating forces, the maximally extended axial period remains at its newly acquired length only for a fraction of the time necessary for a photographic exposure and ruptures almost immediately.

In an electron microscopic study on the extensibility of collagen, in order to eliminate the necessity of depending on the unpredictable and uncontrollable pulling effect of the supporting system, collagen fibrils were manually stretched in water, quick-frozen and dehydrated from the frozen state.

Method and Results

A longitudinal section was made in a segment of rabbit tendon freed from its peritenon, and a few fibers were pulled away. Transferred to a clean glass slide they were teased under triple-distilled water to a very thin layer of tissue wide enough to cover the supporting metallic screen and extending beyond it by at least $^1/_4$ of an inch. One edge of the preparation was frozen with a small piece of dry ice so as to fix that portion of collagen to the glass slide. The CO_2 gas evolved at this stage would have obscured the field of vision had the tissue not extended beyond the screen for some distance. A glass slide was preferred to a metallic one because of the former's low thermal conductivity which prevented immediate freezing of the whole specimen when dry ice was applied to only one portion of the tissue. One edge of the tissue was thus securely fixed; the other was pulled so as to stretch the collagen fibers. The force was applied along the whole free edge in order to avoid curling and folding over of the prepared tissue. While the collagen was kept under tension, the specimen was rapidly frozen by the direct application of dry ice.

A polished brass block precooled in a mixture of dry ice and acetone kept the glass slide and specimen frozen while the collagen was dehydrated under a bell jar connected to a vacuum pump. The dried preparation was removed from the vacuum system when it was estimated that it had regained room temperature, in order to prevent atmospheric water vapor from condensing over it.

When examined in the electron microscope it was apparent that, while a few fibrils were unaffected by the procedure and some had ruptured, the constituent axial periods of the majority had elongated to various extents. Enormous increments could then be photographed and directly measured. Since one could judge from the image cast by the axial periods on the fluorescent screen whether or not they had elongated appreciably, those which had not were easily detected and discarded for the purpose of this investigation. Photographs were consequently taken only of those fibrils whose axial period displayed a considerable lengthening: 75 such fibrils were so studied. The

longest period (Fig. 1) measured was 7000A, as close by as could be determined. This finding was noticed once in two separate fibrils. As noted previously [4], the demarcation between light and dark portions of the macroperiod became less distinct in proportion to the elongation of the period.

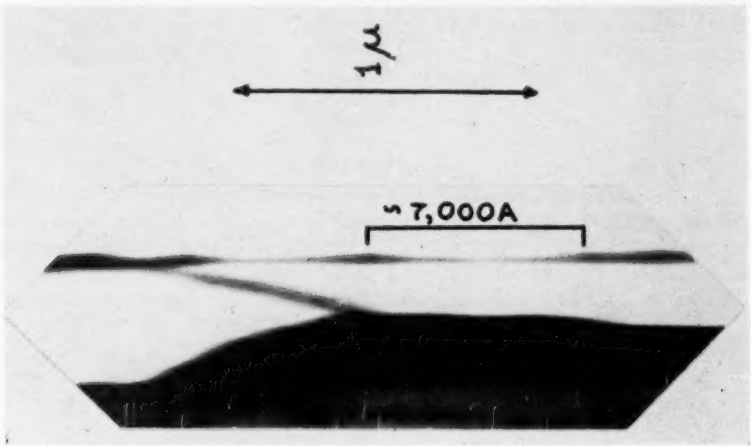

FIGURE 1.—Electrom micrograph of hydrated collagen, manually stretched, and dehydrated from the frozen state.

Comment

It is generally accepted that in the polypeptide chain of collagen the chemically individualized 419 constituent amino acid residues are placed at intervals of 2.85A from each other. The theoretical but unattainable length of a completely unfolded chain would be of approximately 1200 Å [5]. If 7000Å is taken as a correct value for the maximal extensibility of an axial period of collagen, in order to account for this observed increment it seems logical to infer that at least 6 individual polypeptide chains are linked in series within the overall length of a micelle. This figure corresponds to the number of elevations resolved with photodensitometric methods (Fig. 2) in shadowed but non-stained collagen fibrils (Fig. 3). Under this assumption each intraperiodic elevation may represent the projection of a single, folded up constituent polypeptide chain.

Dehydration from the frozen state is not a novel method of preparing tendon for electron microscopy [7], but apparently this is the first report concerning its use as an adjuvant to the study of the extensibility of the constituent axial periods.

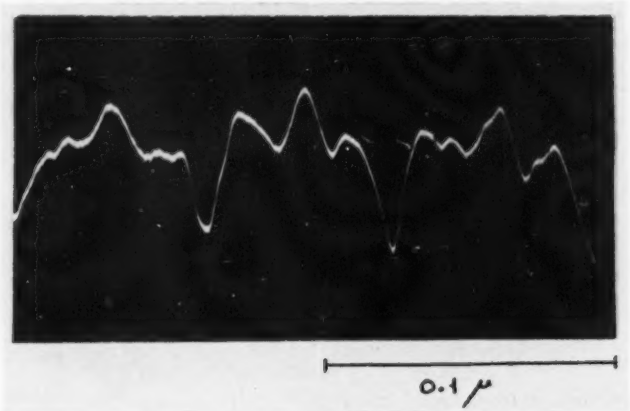

FIGURE 2.—Pattern obtained from the photodensitometric analysis of an electron micrograph of shadowed collagen. Three periods are represented: six elevations are visible in the one at the right.

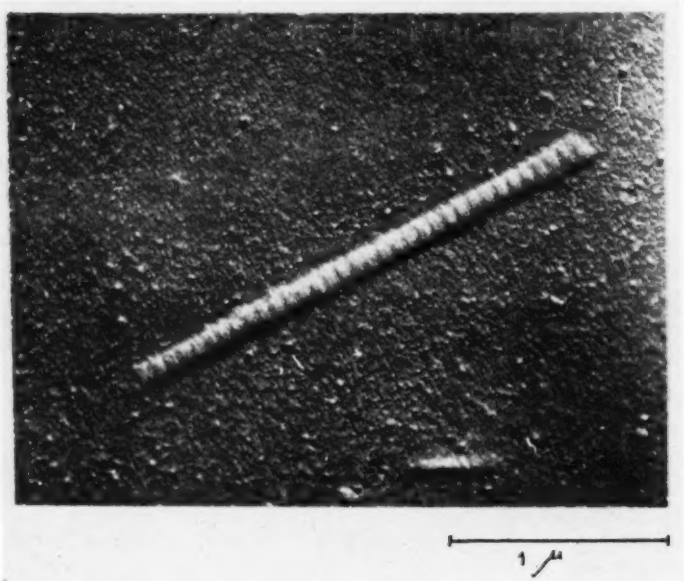

FIGURE 3.—Electron micrograph of a segment from a fibril of collagen. (Shadowed with palladium).

The hydration centers in the polypeptide chain are probably represented by the oxygen and nitrogen atoms capable of forming hydrogen bonds with water molecules [3]. When water is bound the long fiber-axis period is elongated, and the distance between side chains is increased as evidenced by the difference in the x-ray diffraction pattern of dry and wet collagen [1, 2]. Conversely, dehydration in air by bringing adjacent polypeptide chains closer together may increase the opportunity for the establishment of additional cross-linkages. This would tend to stabilize the chains in their new steric position and help them resist unfolding when a mechanical force is applied. The method described above eliminates the possible hindrance to elongation associated with air-drying.

SUMMARY

Stretched collagen fibrils have been lyophilized and examined in the electron microscope. With this method it has been possible to measure on electron micrographs elongations not previously reported. The possible significance of the obtained values is discussed.

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Synthetic Fat Replacement Materials for Leather

III. INTRODUCTION; OBJECTIVES; A GLOSSARY OF GERMAN EXCHANGE FATS

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INTRODUCTION, OBJECTIVES AND DEFINITIONS

A study of German exchange fats for leather was begun in this laboratory in May, 1946, following contractual arrangements between the U. S. Department of the Army (Quartermaster General's Office) and the Ohio State University Research Foundation through the National Academy of Sciences.

Project 50 was concerned with the several phases of leather research being conducted at a number of institutions under the coordinatorship of Dr. Fred O'Flaherty of the Department of Tanning Research at the University of Cincinnati. Specifically, Project 50-E was set up to study the fat substitutes devised by German industry for use in leather technology. In 1947 the leather research program was re-organized. Project 50-E became QMC Project 54-46 and was placed in the category of stragetic and critical materials because of the world shortage of fats and oils which prevailed at that time. A description of the QMC research program for leather has been recently published [1] by Dr. S. J. Kennedy, Research Director of the Textile, Clothing and Footwear Section, Research Development Branch, Military Planning Division of the QMC. Dr. Kennedy has counselled with us throughout the project and we are greatly indebted to him for his numerous contributions to the work. The project has been underway continuously since 1946 and terminated in September, 1950.

The present paper and several to follow include data and information taken from our final report to the Quartermaster General on Projects 50-E and 54-46. Two preceding papers [2, 3] were mainly descriptions of the behavior of certain exchange fat analogues in actual leather processing, work which was done in Dr. O'Flaherty's laboratory.

In anticipation of and during the course of the war the Germans in the face of serious shortages of fats, oils and waxes and allied materials, developed numerous substitutes which were designed to replace these materials as foods, as detergents, as protective coverings and as lubricants. In line with these developments fat replacement materials were devised for fat-liquoring, stuffing, oiling and finishing leather. In order to avoid the innuendo of the expression "substitute" (Ersatz) these materials were designated as "exchange fats" (Austauschfettstoffe). From time to time, reports from German tanners came to us that the replacement materials were being used successfully and were one of the reasons for the superior durability of the Wehrmacht shoes over those supplied to the U. S. army, leather from the latter having been stuffed with natural fats. In view of these allegations and in order to study and make available to American tanners and especially the Military Services those products which possessed merit from the numerous German exchange fats, the general objectives of the present project may be stated as follows:

(1) To make a literature search of German exchange fats;
(2) To examine authentic specimens of these materials so far as they were available;
(3) To synthesize analogues of these materials from raw materials which are commercially available in the United States.
(4) To develop new material for the American leather industry and, more specifically, materials for the Military Services.

Acting in close cooperation with the problems undertaken at The Ohio State University the personnel of the Tanners Council Laboratory at the University of Cincinnati have performed the invaluable service of screening many of the synthetic analogues on a small scale in leather, and of testing the leathers so produced. Without this cooperation most of our progress would have been impossible. In addition, the consulting services of Mr. W. T. Roddy, and Drs. R. M. Lollar and Fred O'Flaherty have been constantly available and have been responsible in large part for the direction in which the project has developed.

The fats and oils are naturally occurring glycerides of the fatty acids. Lipids comprise a more general class of substances. They are, by definition, naturally occurring substances which are soluble in the organic solvents, or, better still, they are the fatty acids and their naturally occurring compounds. The expressions "exchange fats," "Synthetic lipids," and "synthetic fats" as employed in the present report are misnomers because, with almost no exceptions, these materials are not chemically related to the true lipids and the fats and oils. Chemically, the exchange fats comprised such materials as hydrocarbons, aliphatic sulfonyl chlorides, polyvinyl ethers and the like. It is true, on the other hand, that from the intermediate and wax fractions of Kogasin, synthetic crude oil, the Germans devised methods for the synthesis of fatty acids and glycerides which actually came into limited use as food fats.[4, 5, 16]

A GLOSSARY OF GERMAN FAT REPLACEMENT MATERIALS FOR LEATHER

Principal Sources of Information:

The first information which was made available to us in conducting this investigation was the report (APO 757) of G. W. Schultz and Adolph Schubert to the Quartermaster General[6]. These highly qualified leather technologists visited Germany at the conclusion of hostilities with the object of "making available the technological processes used by German tanners, giving special attention to those used in making leathers for the Wehrmacht." Their report was also concerned with the production and use of synthetic tannins, synthetic oils, and other important materials used in the manufacture of leathers. The main body of their report is important, so far as exchange fats are concerned, only in so far as it includes the comments of a number of German tanners on their success, or failure, in the use of these materials. The report states that after 1941 the use of these materials was mandatory with the tanners, but it was common practice to use them in 50-50 mixture with natural fats. The master copy of this report included 18 pages of so-called production sheets[7] which gave important details concerning the manufacturing processes for Derminolnarben oil, Mersol H (Immergan), Derminol oils 1 and 2, Derminollicker 1 and Derminol fat 2. These details

were extremely valuable in conducting our program. From other reports we were able to arrive at the composition of the Densodrins and Immergan, the latter being an extremely important oil tanning agent. Both Schultz and Schubert, in particular, have met often with us and the Cincinnati group to discuss the development of the program. We wish to acknowledge this invaluable assistance.

Further important information was obtained from a copy of Gnamm's "Die Fettstoffe des Gerbers,"[8] published in Germany during the war and loaned to us by Dr. Schubert. Brief descriptions of 27 different products are to be found in this book, but practically no details as to their chemical composition are given. This book also lists a large series of trade products for leather, which we have not included in our report because their ingredients were mainly natural fats and oils.

Additional information on exchange fats, again vague in details of chemical composition, but with valuable data on physical and chemical properties and information on actual formulations in leathers, was found in two trade booklets published by I. G. Farbenindustrie entitled "Der Austausch von naturlichen Fetten, Olen und Wachsen"[9] and "Austauschfettstoffe fur Leder."[10] An original copy of the latter was loaned to us by Schubert. A translation of "Austauschfettstoffe fur Leder" was later issued by O.T.S. as Leather Series Report No. 4[11], and entitled "The Tanigan Extra Stuffing Materials." (See also (11a).

A series of four papers[12, 13, 14, 15] entitled "Uber neuere Produkte fur die Lederfettung" by Herfeld et all was published in "Collegium" in 1942-3. Photostats of these were available soon after the project was begun, but little specific information on chemical composition was contained therein. As the work progressed, further important details came to us from time to time through various Department of Commerce reports.

The Glossary:

There is listed below in alphabetical order a large number of German fat replacement materials which were suggested for or actually came into use as fat replacement materials in leather. There are included in this Glossary, when known, names of manufacturers, chemical nature, and chemical and physical properties. The list is fairly complete and includes all of the exchange fats which came into use in significant amounts. These latter are designated by an "*" in front of the name. Products thus designated are described in more detail later.

ALCOHOLS, FATTY[5, 16, 17] I.G.F.

Fatty alcohols, mainly C_{11-18}, were made by the O.X.O. process[17] which consisted of treatment of Fischer-Tropsch olefinic 'gatsch' with CO and H_2 under high pressure. The alcohols were sulfated to obtain non-soap detergents and were used for other purposes.

ANTI-FOAMING AGENT G. M.[18]
Composed of 50% Mepasin and 50% Mersolats H and D. I.G.F.

ANTIOXYDUL[8, 14] Zschimmer and Schwartz
A yellow-brown, clear oil, possibly identical with Geledol S-42. Properties: 35.8% volatile at 100°C. [1]after 20 hrs.; 3.4% ash; 0.004% Fe_2O_3; pH of water extract, 5.2; mixes with water in all proportions. Possibly a sulfated castor oil. Used as an oil for making vegetable tanned leathers.

APPRETAN WL CONC.[19] I.G.F.
A 50% aqueous solution of Igevin M-40.

APPRETAN WL 25[19]
A 25% aqueous solution of Igevin M-40.

APPRETUR SS[8, 13] Röhm and Haas
A water solution of synthetic resin. Analysis: 5.5% solids; 1.5% ash; pH of water soln., 7.28. Used as a substitute for soap in the manufacture of grease, especially for russet leather.

AVIROL[6, 20] Hely'sche Lederwerke Liebenov, Worms.
A sulphonated fatty alcohol, used in place of egg yolk.

*CHLOROKOGASIN[21] See Derminolnarben oil.

CHLOROMEPASIN[22, 23, 24] I.G.F.
Derivative of Mepasin (hydrogenated Kogasin II). See Kogasin II.

COREPALE K[25] I.G.F.
The reaction product of technical xylene, formaldehyde and acetophenone. Used in combination with nitro cellulose lacquers for finishing leathers.
(1) All temperatures hereafter are in °C. unless *otherwise noted.*

COREPALE W[25] I.G.F.
The reaction product of Weichharz XF (medium viscosity), adipic acid-trimethylpropane, and p-toluene sulfonchloride.

CORIPOL EM[8, 13] Chem. Fabrik Stockhausen
A water soluble, mobile bluish colored liquid. Properties: 16.5% volatile at 100°; 2.7% ash; 0.002% Fe_2O_3; acid no., 1.5; pH of water extract, 9.5; soluble in diethyl and petroleum ethers. Recommended as a liquor oil for chrome leather. According to tests it is qualified for the oiling of vegetable tanned leather directly as well as in 1: 1 water dilution. Especially recommended for soft leather goods.

CORIPOL K 42[15] Chem. Fabrik Stockhausen

A brown colored emulsion. Properties: 18.8% volatile material at 100° after 5 hrs.; 81.2% solids, having a 10.3% ash content of which 0.003% is Fe_2O_3; pH of aqueous extract, 5.63. Useful as a liquor oil. Forms stable, milky emulsions with water, even at 100°. Leather, thus treated is indistinguishable from that normally fat-liquored.

CORIPOL M[8,13] Chem. Fabrik Stockhausen

A mobile dark brown liquid, forming stable emulsions with water. Composed of a water soluble mineral oil sulfonate with 80% lipid content. Properties: 14.9% volatile material at 100°; 85.1% solids of which 4.9% is mineral matter containing 0.002% Fe_2O_3; pH of water extract, 8.09. Recommended alone or combined with liquors for chrome leather and as a substitute for the customary fat-liquor oils.

CUTAPOL[6] Böhme

A successful substitute for cod oil, used in the production of German Army sole leather.

CUTAPOL M[8] Böhme

A sulfonated mineral oil with added wax esters. Properties: 85% total lipid; 2.0% SO_3; pH, 6.6. Employed as a tanning oil and as a leather fatting agent.

CUTAPOL O[8] Böhme

Sulfonated mineral oil with added lipid. Properties: 89% total fat; 3.6% SO_3; pH, 8.0. Used as a substitute for train (fish) oil and degras. Yields an emulsion with water.

CUTISAN BS[26] I.G.F.

Properties: Total lipid, 82-84%; water, 3.8%; water emulsion capacity, 41%; unsaponifiable, 0.; pH 4.8. Produces a milky emulsion of good stability.

CYCLANON (Cyclanon LA conc. paste)[8,10,18,22] Böhme

A paste similar to Derminol A conc. (IG). and Smenol WO (Böhme). A reaction product of cocoanut oil alcohols with chlorosulfonic acid. May contain sulphonated sperm oil alcohol. Could be made from O.X.O. alcohols. Used as an auxiliary material, (wetting and dispersing agent) in oiling harness and russet leather and in liquors for upper, portfolio, and clothing leathers. CYCLANON WN is used double conc. as an auxiliary material in soaking and liming.

CYCLANON LA CONC.[16] I.G.F.

Prepared from cocoanut oil alcohol and chlorosulfonic acid. See also Cyclanon.

CYCLANON OA PASTE [22,23] I.G.F.

A fatty alcohol sulfate type detergent, the fatty alcohols being produced by the reaction of C_{11-17} Fisher-Tropsch fractions with water gas at high pressure (O.X.O.) in the presence of cobalt-thoria-magnesia catalyst to produce aldehydes; and reduction of the aldehydes to alcohols with hydrogen in the presence of the same catalyst.

DENSODRIN AW [10,11] I.G.F.

A soft, liquid resin, used for impregnating leather.

DENSODRIN H [19,27] I.G.F.

A mixture of polyvinyl lauryl ether and rosin.

DENSODRIN HO $^1/_{148}$ [22,28] I.G.F.

A dark, highly viscous oil. The condensation product of reacting one mole of xylol with one mole of ethylene chloride. Soluble in mineral oil, and the usual solvents. Suitable for impregnating leather.

DENSODRIN HO $^1/_{148}$ (product analogous to) [10,22,28] I.G.F.

A soft sticky resin. Condensation product of 2 moles xylol reacted with 1 mole sulfur chloride. Product in experimental stage, submitted as Densodrin substitute and as constituents of a Degras.

*DENSODRIN NH [9,10,11,19,20,27] I.G.F.

A dark resin. A polymer of B-decahydronaphthol vinyl ether. (See next paper).

*DENSODRIN NW [9,10,27,20,11,11a,26] I.G.F.

K-value approximately 25. Used in preparation of sole leather and in the impregnation of upper leather. (See next paper.)

DENSODRIN V [19,27] I.G.F.

A polyvinyl cetyl ether.

DENSODRIN W [19,27] I.G.F.

Prepared by copolymerization of 70% vinyl isobutyl ether and 30% vinyl lauryl ether.

DERMINOLS A and B [8,10,11,20] I.G.F.

Composed of neutral fatty alcohol sulfonates. Employed as supplements in fat liquoring and greasing. They aid fat take up and distribution in the leather and are recommended for vegetable tanned leather. (See Cyclanon LA conc. paste)

*DERMINOL DEGRAS-1 [11,11a] I.G.F.

An ochre-yellow, salve-like substance, composed of a select group of esters which are chemically related to the natural fats and which contain oxygen rich groups and active residual valences.

DERMINOL L [10,11] I.G.F.

A yellowish paste, similar in properties and use to Igepone A; made from a cod oil base.

DERMINOL I [6].

Used with soap and a small amount of neatsfoot oil in the fatliquoring of goat skins.

*DERMINOL FAT 1 [8,12,27] I.G.F.

A brown material of salve-like consistency. Composed of chlorinated high molecular weight hydrocarbons.

*DERMINOL FAT 2 [6,7,8,9,10,15,27,22,29,11,11a)] I.G.F.

A brown product of vaseline like consistency, composed of chlorinated paraffin wax, (6% Cl), and Derminolnarben oil.

DERMINOL FAT Hö $^{1}/_{146}$ [28] I.G.F.

A light tallow-like product which is easily absorbed by leather. 70 parts Derminol oil Hö $^{1}/_{142}$ and 30 parts of a chlorinated paraffin, containing 6% Cl. Substitute for greasing leather. Imparts water resisting properties to leather.

DERMINOL FAT Hö $^{1}/_{153}$ [28] I.G.F.

70 parts Derminol oil Hö $^{1}/_{151}$, and 30 parts chlorinated paraffin (6% Cl).

*DERMINOLLICKER 1 [6,7,8,9,10,13,27,22,18,11,11a] I.G.F.

A mixture of 28% Mepasin, 7% Mepasin sulfamide, 20% Mepasin sulfamido-acetic acid, 20% water, and 25% Derminolnarben oil.

DERMINOLLICKER 2 [8,13] I.G.F.

A brown, mobile liquid with a weak ammoniacal odor; soluble in diethyl and petroleum ethers. Properties: 82.1% solids of which 73.7% is unsaponifiable; acid no., 13.3; pH of water extract, 6.24; emulsifiable with water, a 5% solution producing an emulsion stable for several hours; heating to 100° causes only slight separation. Used in the fat liquoring of chrome leather.

*DEMINOLLICKER P [10,11,11a] I.G.F.

A dark brown, syrupy, water-miscible oil.

*DERMINOLNARBEN OIL [6,8,10,15,22,27,21,11,11a] I.G.F.

(See leather oil $^{1}/_{90}$).

A clear yellow, mobile liquid soluble in ether and petroleum ether. Mepasin, chlorinated to 40% Cl.

*DERMINOL OIL 1 [7,8,9,10,27,11,11a] I.G.F.

A mixture of 70-80% Derminolnarbenol with 20–30% polyvinyl isobutyl ether.

*DERMINOL OIL 2 [7,8,10,13,27,26,25,11,11a] I.G.F.
A viscous dark brown oily liquid which remains clear even on long standing. Made by condensing xylene, formaldehyde and a C_8-C_{10} alcohol fraction.

*DERMINOL OIL 3 [10,11,11a] I.G.F.
A pale yellow, clear oil, composed of a high molecular weight aromatic ester.

DERMINOL OIL Hö $^1/_{142}$ [28] I.G.F.
Made by reacting 1 mole ethylene chloride with 2 mols of xylol with $AlCl_3$ as a catalyst. Properties: 5% volatile at 100° in 7 hrs; viscosity 60 sec. (Fordbeaker 20°).

DERMINOL OIL Hö $^1/_{143}$ [28] I.G.F.
Composed of 80 parts of Derminol oil Hö $^1/_{142}$ and 20 parts Igevin J-30. Superior to Hö $^1/_{142}$ because of better water proofing qualities.

DERMINOL OIL Hö $^1/_{149}$ [28] I.G.F.
A light tallow-like product, prepared by mixing 70 parts of Hö $^1/_{142}$ and 30 parts of chlorinated paraffin (6% Cl). Easily absorbed by leather, making it water resistant and giving it a finish similar to tallow.

DERMINOL OIL Hö $^1/_{151}$ [28] I.G.F.
A reddish, brown oil, prepared by reacting 1 mole of sulfur chloride with 4 moles of xylol. Propoerties: 1-2% volatile at 100°; Fordbeaker viscosity, 40 sec. at 20°.

DEWANIL 1542. [22] I.G.F.
Prepared from paraffin and various synthetic fats and resins.

EMULGATOR Hö $^1/_{136}$ [22,18]. (see EMULPHOR STU) I.G.F.

EMULGATOR MK [18] I.G.F.
60% Mersolat H paste.

EMULGATOR M [18]. (see EMULPHOR STU) I.G.F.

EMULGATOR MW [18] I.G.F.
70% Mersolat H paste.

EMULGATOR STENOLAT C GA [15] Böhme Fettchemie
Properties: 6.8% solids; pH of a solution of 10 gms. per 100 cc water, 6.3; no free strong acids or alkalies. Useful for oiling chrome and vegetable tanned leather. A useful emulsifier, but contains a colloid which tends to coagulate in the acid range injuring the stability. Lowers water resistance of leather.

EMULGIERWACHS P [9,12,26] I.G.F.

A stable, wax-like solid. Prepared by the oxidation of hard paraffin. Contains fatty acid esters, estolides, alcohols and high molecular weight paraffins up to C_{50}. Properties: 2.9% volatile at 100°; 0.1% ash; nearly complete absence of injurious iron compounds; sap. no. 83.00; acid no., 34; melting point, 80–88°; hardening point, 64°; pH of aqueous extract, 4.34; no free strong acid or alkali; soluble in CCl_4; partially soluble in petroleum and ethyl ethers. Supplied in two forms: unsaponified as a tallow exchange product; saponified for Fahlleather stuffing. Replaces tallow satisfactorily up to 33%, being somewhat more water resistant.

EMULGIERWACHS PS [8,15] I.G.F.

A yellow-brown sticky solid. A synthetic fatty acid ester. Properties: 3.5% volatile at 100° after 5 hrs.; 0.2% ash; 0.004% Fe_2O_3; sap. no., 73.3; acid no., 37.5; no free strong acids or alkalies; pH of water extract, 4.87. A partial substitute for tallow; further substitution above 30-40% is inadvisable. It is also used as a soap substitute in russet leather oiling.

EMULGIERWACHS PVS [15] I.G.F.

A brown, sticky wax, composed of the saponified form of Emulgierwachs PS. 8.9% volatile at 100° after 5 hrs.; 7.5% ash; 0.004% Fe_2O_3; pH of water extract, 8.94. Can replace soap in chrome leather liquors and in the soap greases of russet leather (fresh side). Lowers water absorbability, increases body and "stand".

EMULPHOR ELO [18] I.G.F.

Reaction product of Mesamide H, SO_2 and formaldehyde.

EMULPHOR O [22] I.G.F.

A polyglycol ether, obtained by reacting 20 moles ethylene oxide with sperm oil alcohol.

EMULPHOR STH [18,30] I.G.F.

33–37% sodium mepasin sulfamido-acetate, etc. (See Deminollicker 1).

EMULPHOR STU (See Derminollicker 1). [18,30] I.G.F.

EMULPHOR STX [18,30] I.G.F.

Potassium salt of dodecyl (C_{12}) xylene sulfonic acid.

ESTE-LICKER BS 2018 [15] Chem Fabrik Stockhausen

Light brown, very mobile liquid. Properties: 47.9% volatile at 100° after 5 hrs; 7.4% ash; 0.003% Fe_2O_3; pH of water extract, 4.70; free from strong acids and bases; forms stable water emulsion even at 100°. Can be used in fat liquoring, especially for very soft leather.

ESTE-LICKER MS [8,14] Chem Fabrik Stockhausen

Dark-brown colored, very mobile liquid. Properties: 27.1% volatile at 100° after 5 hrs.; 3.8% mineral content; 0.007% as Fe_2O_3; acid no., 8.5; iodine no., 12.1; no free strong acids or alkalies; forms emulsions with water which are stable at 100°. Used in the fat liquoring of chrome leather.

EUKANOL [22,20] I.G.F.

Finishes for leather, which contain casein, shellac, montan wax, and synthetic resins.

EUKANOL OIL C [18] I.G.F.

Composed of 20% NH_4 Mepasin sulfamido-acetate, 7% Mepasin sulfamide, 40% Mepasin, 25% chlorinated Kogasin, 8% H_2O. (Similar to Derminollicker 1). Used for oiling leather.

FATTY ACID ETHANOLAMINE SULFATE [22] I.G.F.

Prepared by the sulfation of a synthetic fatty acid ethanolamide with a sulfation mixture of chlorosulfonic acid, formamide and urea.

FATS—SYNTHETIC FROM FISCHER-TROPSCH I.G.F.

PARAFFIN [9,22]

Description of oxidation of paraffin, (See also Fatty Acids).

FATTY ACIDS [9,22,4,16,29,5,31] I.G.F.

Paraffins are oxidized with air, using $KMnO_4$ catalyst at 130°-150°. Unreacted paraffin removed with alcohol and benzene. Crude fatty acids are steam distilled at 250°. Keto-acids are removed by the Hader process. Glycerol is synthesized from propylene and the fatty acids esterified with glycerol to give synthetic fats.

FETTLICKER AF [15] Chem Fabrik Stockhausen

Brown colored, fluorescent, mobile liquid. Properties: 34.5% volatile after 5 hrs. at 100°; 5.5% ash; 0.003% Fe_2O_3; pH of water extract, 7.07; forms stable water emulsions even at 100°. A substitute for other materials in the oiling of "boxleder," reduces the surface gloss and "stand" negligibly. Increases stability and water-resistance of leather.

FETTLICKER GRUNAU [8,14] Chem Fabrik Grunau A. G.

A light brown, very mobile liquid, composed of a protein-fatty acid condensation product; contains no mineral oil sulfonates. Properties: 31.7% volatile at 100°. after 5 hrs.; 0.003% Fe_2O_3; pH of water extract. 7.94; no free strong acids or alkalies; forms stable emulsions with water even at 100°. Used as a fat-liquor.

GARDINOL [23] Böhme

Fatty alcohol sulphonate type detergent. A high pressure type synthesis was used by Bonhme in its production, while I. G. Farbenindustrie used sodium reduction of fatty esters.

GELEDOL P [8] Zschimmer and Schwartz

A mixture of alcohol sulfonates with mineral oil. Employed in oiling chrome-glove leather.

GELEDOL S-42 (Antioxydul) [8,14] Zschimmer and Schwartz

A brown, clear oil. Similar to Antioxydul S-42 in composition. Properties: 35.8% volatile at 100°; 3.4% ash; pH of water extract, 5.2; soluble in water in all proportions. Recommended as a tanning and leather oil for vegetable tanned leather. A neutral product has also been prepared which should be useful as a liquor oil for chrome leather.

GELEDOL S-52 [8,14] Zschimmer and Schwartz

Fluorescent, reddish brown liquid. Properties: 24.3% volatile at 100° after 20 hrs.; 1.1% ash; 0.002% Fe_2O_3; pH of water extract, 5.95; soluble in ether and petroleum ether, contains no free strong acid or alkali; emulsifiable in water being stable even at 100°. Useful in fat-liquoring chrome tanned leather.

GELEVAN [22] I.G.F.

Prepared from Mepasin, Trilon B etc.

HOSTAPON [22,18]

Mepasin sulfonate, made by reaction of SO_2 and O_2 with Mepasin.

IGEPON A [10,11] I.G.F.

A white pasty, anion-active, wetting agent used as a fat-liquoring aid. It possessed good emulsifying and lubricating properties.

IGEVINS [33,34,35] See also the Densodrins I.G.F.

Yellow-brown amber tacky liquids and resinous materials; properties, depending on degree of polymerization.

Vinyl polymers of various types. Polyvinyl ethers which are H_2O-insoluble exhibit good solubility when first dissolved in methanol. White, solid chloro-compounds are possible; they give good stability and can be converted into H_2O-soluble sulfo-acids with sulfites. Careful sulfonation with acetosulfuric acid yields products with detergent qualities. Used as adhesives and for the waterproofing of leather.

IGEVIN A 25 [33,19] I.G.F.

A polyvinyl ethyl ether, prepared by polymerization of monomeric vinyl ethyl ether, with $BF_3 \cdot 2H_2O$ as catalyst; K-value, 15-18. Used as a leather impregnant.

IGEVIN A 50 [19,33] I.G.F.

Prepared by catalytic polymerization. Similar to Igevin A-25, except the K-value is 55-60; water-insoluble; soluble in naphtha and alcohols. Used as a plasticizer for nitrocellulose and natural resin base lacquers.

IGEVIN D [33] I.G.F.

A solid, resinous polyvinyl ether. Soluble in acetone, ether, ethyl acetate, hydrocarbons and chlorinated hydrocarbons. Softening point 70-75°. Used to improve film-fastness and heat resistance of other Igevins.

IGEVIN DJ [33] I.G.F.

Similar to Igevin D except the S. P. is 65-70°.

IGEVIN IL [8,12,26] I.G.F.

Formerly designated Lederol 1239. A viscous, brown oil made by polymerizing vinyl isobutyl ether. Properties: acid no. 0.00; sap. no. 0.01; pH of aqueous extracts, 6.5; soluble in CCl_4, petroleum and ethyl ethers.

IGEVIN J 20 [19, 33] I.G.F.

Similar to Igevin J 30 with the exception that the K-value is 15.

*IGEVIN J 30 [19,33,11a] I.G.F.

Polyvinyl isobutyl ether. Prepared by catalytic polymerization of vinyl isobutyl ether. K value 18-20. Used in leather impregnation.

IGEVIN J 60 [19,33] I.G.F.

Polyvinyl isobutyl ether. K-value 55-60; naphtha-soluble; insoluble in H_2O and alcohol; solubility in ethyl acetate, 70%. Used as a plasticizer.

IGEVIN JZR [19] I.G.F.

80% polyvinyl isobutyl ether and 20% polydekalol vinyl ether. Prepared by the catalytic polymerization of monomeric dekalol vinyl ether and momomeric vinyl isobutyl ether with $BF_3 . 2H_2O$. K-value 18-25. Used as a surface coating for masonry.

IGEVIN M 40 [19,33] I.G.F.

Polyvinyl methyl ether, produced by the catalytic polymerization of vinyl methyl ether; K-value, 45-50; soluble in water and lower alcohols; insoluble in naphtha; solubility in methyl and ethyl acetates, 70 and 50% respectively. Used as a plasticizer for nitrocellulose lacquers, as an adhesive and thickener, and as a textile finishing agent.

IGEVIN Z [19] I.G.F.

May be identical with Densodrin NH.

IGEVIN ZJ [19] I.G.F.

60% polydecalol vinyl ether, 40% polyvinyl isobutyl ether. Prepared by $BF_3 \cdot 2H_2O$ catalyzed polymerization of the monomeric mixture. Properties: at least 10% soluble in naphtha, benzol and methylene dichloride. Softening point 65-70°. Resinous-like substance.

I. G. WAX [9] I.G.F.

Prepared from Montan wax. Used for leather fatting and burning in of chrome sole leathers.

I. G. WAX V [19] I.G.F.

Polyoctadecyl vinyl ether. Properties: M. P., 50°; flash pt. 180°; soluble in 4 parts naphtha.

*IMMERGAN [6,10,13,2,36,36a,11,11a] I.G.F.

Sulfochlorinated Mepasin.

*KOGASIN [7,22,23,21,11a] I.G.F.

Composed principally of straight chain hydrocarbons (avg. C_{16}), boiling 220–320°. Used as the basic raw material for the production of many "exchange fats" for leather.

LEATHER FAT Hö $^{1}/_{123}$ [26] I.G.F.

Composed of chlorinated hard paraffin (m.p., 105°). Properties: 11.2% Cl; acid no. 0; sap. no., 0; pH of aqueous extract, 8.4; soluble in petroleum ether; partially soluble in ethyl ether; m. p. 59°; hardening pt., 56°. Used in combination with train oil and degras.

LEATHER FAT Hö $^{1}/_{124}$ [26] I.G.F.

Chlorinated paraffin. Properties: 7.1% Cl; acid no., 0.00; sap. no., 7.00; pH of aqueous extract 7.5; soluble in CCl_4 and ethyl ether; m.p. 45°; hardening pt., 43°. Used with train oil and degras.

LEATHER FAT Hö $^{1}/_{153}$ [25] I.G.F.

Analogous to Derminol fat Hö $^{1}/_{153}$.

LEATHER FAT Le 254 [26] I.G.F.

Composed of polytetrahydrofuran. Properties: acid no., 2.3; sap. no. 0.0; pH of aqueous extract, 4.0; soluble in CCl_4, petroleum ether and ethyl ether; partially soluble in alcohol; melting point, 30°; hardening pt., 20°. Used in conjunction with train oil and degras.

LEATHER FAT Lu $^{3}/_{142}$ [26] I.G.F.

An oxidation product of Oppauer motor oil. Properties: acid no., 25.00; sap. no., 37.00; pH of aqueous extract, 4.3; soluble in CCl_4 and ethyl ether; partially soluble in petroleum ether; m. p., 35°.; hardening pt., 30°. A substance softer than tallow, which if substituted for tallow in quantities up to 50%, yields a leather equal to that finished with train oil, tallow and degras. It may be used in combination with 10% Emulgierwachs P; leather thus finished has twice the water repellency of normally fat liquored leather.

LEATHER OIL 1239 [9,26] I.G.F.

See Igevin IL.

LEATHER OIL Le 265 [26] I.G.F.

An acid catlyzed condensation product of diethylbenzol with formaldehyde. Properties: acid no. 0.00; sap. no, 24; pH of aqueous extract 4.5; soluble in CCl_4, petroleum ether and ethyl ether. Contains residual valences capable of combining with leather fibers. Imparts good water-proofing qualities to leather.

LEATHER OIL Le 266 [26] I.G.F.

A condensation product of technical xylene with formaldehyde and subsequently condensed with Leuna alcohol. May be identical with Derminol oil 2. Properties: acid no., 0.0; sap. no., 25.0; pH of aqueous extract, 6.0; soluble in petroleum ether, ethyl ether, and CCl_4. Contains residual valences capable of combining with leather fibers; imparts good water-proofing qualities to leather.

LEATHER OIL Wl [26] I.G.F.

See Derminol oil 1.

LEATHER PRODUCTS [28] I.G.F.

A light oil, prepared by condensation of xylol with halogenated methyl xylols. The viscosity of the product may be varied by changing the ratio of reaction compounds. A soft resin condensation product of xylyl chloride can be made. Properties: low volatility; Fordbeaker viscosity, 20–30 secs. at 20°.

LEATHER TREATMENT PRODUCTS [9,4,16] Deutsche Fettsaurwerke

See Also Fatty Acids.

The volatile, water-insoluble fatty acids obtained from the air oxidation of paraffin are useful in leather treatment.

LEDER-AVIROL BLS [8,12] Böhme

A yellow, salve-like material, composed of oils, fats, waxes and synthetic esters; 31 parts Riffette, 20 parts mineral oil, 35 parts exchange products. Properties: soluble in petroleum ether; 9.7% volatile at 100°; 32.5%, unsaponifiable; 54.2%, saponifiable; acid no., 5.7; iodine no. (Hanus), 35-39; pH of water extract, 6.9–7.2; Fettzahl, 86. Employed as a fatting agent for harness leather. It is useable alone as well as in mixtures with animal and vegetable fats and fat substitutes. The product contains an emulsifier which promotes an even, swift penetration into the leather without injuring the water resistance of the leather.

LEDER-AVIROL FA [8] Böhme

A yellow paste. A mixture of colloidal cellulose derivatives, waxlike fatty substances and fatty alcohol sulfonates as emulsifiers. Properties: 61.1% volatile at 100°; 1.1% ash; 0.002% Fe_2O_3; pH of water extract, 4.54; contains no free strong acids or alkalies; capable of water dilution to all proportions with hot water. Employed as a dressing for russet leather, flesh side.

LEDER-AVIROL FST [8,12] Böhme

A yellow-brown, salve-like product, composed of synthetic oils, wax esters of high melting alcohols, paraffins and other hydrocarbons; 40 parts Riffette, 10 parts mineral oil, 50 parts exchange materials. Properties: soluble in petroleum ether; 0.6% volatile at 100°; 0.6% organics insoluble in ether; 29% unsaponifiable; 71% saponifiable; acid no., 8-10; iodine no., (Hanus), 37.8; pH of water extract, 7.76; Leder-Avirol FST possessed a higher consistency than BLS and was especially suited to the oiling of russet leather, water-proofing, etc. By admixture with neutral oils the product can be prepared of any desirable consistency.

LEDER-AVIROL GST [8] Böhme

Composed of 20 parts Riffette, 25 parts mineral oil, 50 parts exchange products. Properties: Fettzahl, 98. Can be mixed with the usual hard fats and waxes and used for hand application as well as for greasing in drums.

LEDER-AVIROL RK 1 [15] Böhme

A mobile, dark-brown liquid. Properties: 15.2% volatile at 100° after 5 hrs.; 36.8% unsaponifiable; 62.3% saponifiable which appears to be partly sulfonates; 3.7% ash; pH of water extract, 6.22; contains no free strong acids or alkalies; a 5% water emulsion is stable for a long time even at 100°. Used as a fat-liquor oil for chrome leather.

LEDER-AVIROL RM [8] Böhme

Composed of 33 parts Riffette, 15 parts mineral oils, 26 parts exchange fats, plus an emulsifier. Properties: pH diluted with 10 volumes water, 6.5–7.0; forms water emulsions which are stable toward salts and acids. The product was used for the greasing of clothing, glove, casing, chamois and similar leathers.

LEDER-AVIROL RO [8] Böhme

A sulfonated synthetic ester oil. Properties: lipid content, 100%; 27% unsaponifiable; acid no., 0.0; sap. no. 135; iodine no. (Hanus) 55.0. Used as a substitute for train and neatsfoot oils.

LEDER-AVIROL WL [8] Böhme

Properties: Fettzahl, 70; forms a stable milk white emulsion with water in every ratio. Used alone or mixed with vegetable, animal, mineral, or exchange oils for the oiling of all upper and fine leathers.

LEDEROL 1239 See Igevin IL and Leather Oil 1239.

LEDEROL $^{1}/_{90}$ [7,22] I.G.F.

This is Derminolnarben oil.

LEDEROL Hö $^{1}/_{90}$ [21,26]

Identical with chlorokogasin and Derminolnarben oil.

LEDEROL 111 [8,14] Bauer, Gaebel & Cie.

A brown-colored, very mobile liquid. Properties: 18.4% volatile at 100° after 20 hrs.; 0.4% ash; 0.004% Fe_2O_3; acid no., 7.0; iodine no., (Hanus), 7.9; pH of water extract, 4.84; soluble in the usual organic solvents; contains no free strong acids or alkalies. Useful as an exchange product for train oil in the oiling of russet leather and similar types. Leather thus treated is hardly distinguishable from normally treated types. May replace train oil wholly or in part.

LEDEROL 215 [8,13] Böhme

A yellow-brown, synthetic oil. Composed of high molecular weight esters of lardy consistency giving it a good filling power. Properties: 14.7% volatile at 100° after 10 hrs.; saponification no., 34.8; acid no., 0.4; iodine no. (Hanus) 12.5; pH of water extract, 5.10; The product was used as an oiling medium for harness and russet leather in the place of fish oil. Substitution up to 30% of the total fat content was recommended.

LEDEROL Hö Lu 296 [26] I.G.F.

See Derminol oil 1.

LEDEROL 1442 [15] J. R. Geigy

A brown, mobile liquid without characteristic odor. Properties: 21.3% volatile at 100°; no ash; acid no., 1.2; sap. no., 34.0; iodine no. (Hanus), 7.2; soluble in the usual organic solvents; pH of water extract, 5.80; no free strong acids or alkalies. Used as a leather oil for vegetable tanned leather in place of train oil. The finished leather is indistinguishable from that which is normally treated.

LEDEROL CY [8,12] Oranienburger Chem. Fabrik

A viscous non-transparent material, prepared from high molecular weight raw materials. Stable towards salt, alum and chrome; tolerates heat up to 70°; alone or in mixtures of other oiling agents it is a cream-like, stable emulsion. Used especially as a substitute for egg yolk and designated as a special fatting agent for the glove and fine leather industry.

LEDEROL KL CONC. [8,12] Oranienburger Chem. Fabrik

A mobile, water emulsifiable liquid, composed of a fat free sulfonation product; emulsifiable with water; 9.0% volatile at 100°; 0.8% ash; 83.5% unsaponifiable; acid no., 0.5; pH of water extract, 7.36. Used as a substitute for sulfonated oils in the oiling of chrome leather and as a train oil substitute for harness and russet leather.

LEDEROL L 215 [8] Böhme

A clear, yellow-brown oil. Similar to Lederol 215, except that the high melting esters have been removed by cooling and filtering; 5.4% volatile at 100°. Used in stuffing leathers. According to prevailing tests it appeared feasible for use as a fat-liquoring oil for upper leather.

LEDEROL W-1 [26]
See Derminol oil 1.

LICKEROL [6] Böhme
A fat-liquor used for chrome uppers.

LORIKOL [6] Böhme
Used in the tanning of upper and fine leathers. Some manufacturers stated that it produced a white chamois without bleaching that was superior to those produced by either cod and fish oil or by Immergan.

LICKEROIL E-1 See Lickeroil Hö $^{1}/_{102}$ I.G.F.

LICKEROIL Hö $^{1}/_{102}$ [26] I.G.F.
Composed of Mepasin Sulfamidoacetic acid, Mepasin, and Chlorokogasin. Similar to Derminollicker 1. (Trade name, Lickeroil E-1) Properties: Fettszahl 81; water, 15%; unsaponifiable, 63%; pH, 4.7; produces an opalescent water solution of good stability.

LICKEROIL Lu $^{3}/_{138}$ [26] I.G.F.
Composed of Phenylmepasin sulphonate. Properties: Fettzahl 95%; water, 1.4%; water emulsion capacity, 13%; unsaponifiable, 83%; pH, 7.9; produces a milky-white emulsion of good stability.

LUPHENE [22] I.G.F.
Prepared from phenolic resin, Weichharz AT, AT Cellulose and solvents.

LUPHEN, AT, AM, and AW [22] I.G.F.
Varied mixtures of phenol-formaldehyde resin, Weichharz AT and AT Cellulose B of medium viscosity.

LUPHEN, B and BT [22] I.G.F.
Composed of Alkyphen, Weichharz AT, citric acid, AT Cellulose (medium viscosity), Butanol H, xylene and denatured alcohol.

LUPHEN, ST, SM, and SW [22] I.G.F.
Varied mixtures of xylenol resin, Weichharz AT and AT Cellulose B. (medium viscosity).

*MEPASIN [7, 23, 26, 11a] I.G.F.
Prepared by the catalytic hydrogenation of Kogasin. Contained saturated, straight chain, aliphatic hydrocarbons of the C_{16}-C_{20} series. Used as a basic raw material for several surface active agents, detergents, and leather oil exchange products.

MEPASIN SULFOAMIDOMETHANE-CARBOXYLIC & SULFONIC ACIDS [22] I.G.F.
Synthesized by the condensation of formaldehyde with sulfurous acid and sulfamides, or with formaldehyde and HCN. etc.

*MERSOL-D [23, 20, 17, 37, 38, 5, 18, 11a, 32] I.G.F.

A mixture of aliphatic sulfonyl chlorides, produced by the full sulfo-chlorination of Mepasin. Contained 50% mono-sulfonyl chloride, 30% di-sulfonyl chloride, and 20% unreacted Mepasin. Used as a washing agent, when saponified, and as Immergan.

MERSOL H [7, 23, 20, 37, 32, 38, 5, 18, 11a] I.G.F.

Composed of partly sulfochlorinated Mepasin. An intermediate in the synthesis of Derminollicker I.

MERSOL 30 [17, 5, 18] I.G.F.

The same as Mersol H except that only 30–33% of the Mepasin is converted to sulfonyl chloride with a corresponding increase in monosulfonylchloride and unreacted Mepasin.

MERSOLAT D [20, 37, 32, 5, 18] I.G.F.

Composed of the sodium salt of Mersol D, prepared by saponification of Mersol D at 70° with 10% NaOH solution. Used as a soap substitute.

MERSOAT H [23, 20, 37, 32, 38, 5, 18] I.G.F.

Composed of the product of saponification of Mersol H. All unreacted Mepasin is removed. Used in various forms as a soap substitute.

MERSOLAT H 30 [18] I.G.F.

The hydrolysis product of Mersol 30. Has a low salt content and all the unreacted Mepasin has been removed.

MERSOLAT MK [18] I.G.F.

A Mersolat H which is salt free and which has been 70% concentrated.

MESAMIDE E [18] I.G.F.

Composed of Mesamide H., from which the unreacted Mepasin has been removed.

MESAMIDE H [18] I.G.F.

The amide of Mersol H, produced by reacting NH_3 with Mersol H. It contains all unreacted Mepasin and 10% sulfimide. Used as an intermediate in producing various emulsifiers.

MESAMOLL H [18] I.G.F.

The phenyl ester of Mersol H.

MESAPON N [18] I.G.F.

Same as Mersolat D.

MONTAN WAX [9, 39] Riebeck

A dark-brown, hard wax. Prepared from the benzene-alcohol extract of mid-German bituminous brown coal. Contains 16% resinous materials, 14% asphalt, 50% wax esters, and 20% free wax acids. Used as the chief raw material for the preparation of I. G. Waxes.

NEKAL A [23]

Composed of the sodium salt of diisopropyl sulfuric acid. Has good wetting properties and is resistant to hard water.

NUVA OIL [22] I.G.F.

Contains Emulphor O and Lauryl sulphate.

OILS, SYNTHETIC EDIBLE, RESUME' OF PROCESS [22] I.G.F.

The raw materials for the process are C_6-C_{25} fatty acids. The high boiling fraction containing ketonic and hydroxy derivatives is too dark for use and the C_6–C_{10} fraction with a low viscosity cannot be used. Both even and odd carbon chains may be used. A small portion of hydroxy and dicarboxylic acids is removed.

PELZWASCHMITTEL LM [8] I.G.F.

Used as a degreasing agent for sheep skins and many varieties of goat skins.

PELZWASCHMITTEL WP [8] I.G.F.

Composed of fatty alcohol sulfonates which are manufactured according to DRP 592569. Employed for the washing of fur and similar skins. The product possesses a powerful wetting action and emulsifies dirt, fat, and similar materials.

PERENIN EH [8] Böhme

Fatty alcohol sulfonates which are mixed with emulsifying or dispersing agents. Used as an emulsifier for fats and oils. It facilitates the fat up-take in fat-liquoring processes.

PHENYLMEPASIN [22, 23, 24] I.G.F.

A derivative of Mepasin (hydrogenated Kogasin II). See Kogasin II.

PHENYLMEPASIN SULPHONATE [22, 23, 24, 26] I.G.F.

Prepared from the reaction of Chloromepasin and benzene in the presence of iron free from Al; the phenylmepasin is then sulfonated and neutralized with caustic soda.

*RB-HARD WAX [7, 29] I.G.F.

A high melting wax from Kogasin.

RASCHIT [6]

A chlorinated naplathalene, used in preserving leather.

SAPIDAN LN CONC. [8] Böhme

A yellow liquid. An alcohol sulfonate which is manufactured according to DRP 592569. Properties: Gives a clear water solution; stable in the presence of acids, lime and hard water; aids in the absorption of fat giving a homogenous fat distribution. It is employed for the rubbing up of the grain, and the fulling of suede leather.

SEPROL [8] Böhme

A fatty alcohol sulfonate processed according to DRP 592569.

SMENOL AL [8,13] Böhme

A yellow-brown liquid. A fatty alcohol sulfonate containing dissolved fat. Properties: total fat, 30%; acid no., 0-3; sap. no., 10-15; iodine no., 0-5; pH of 10% solution, 6.5–7.0. Employed as an emulsifier for leather oiling in place of soap and degras. Also used as a degreasing agent in mixtures with fat in organic solvents.

SMENOL V. [8] Böhme

A bright yellow, medium viscosity liquid. Properties: 50% sulfonate; iodine no. (Hanus), 0.5; pH of a 10% solution; 6.4–6.8; stable in the presence of acids, alkalies and synthetic tanning agents. Recommended as an auxiliary material for tanning. It hindered mold formation and due to its dispersing power the formation of slime was also hindered. It buffered the acidic vegetable tanning liquors and appeared to accelerate the thorough tanning of the skin. It clarified the grain color and improved the grain elasticity and tensile strength of the leather. No bleaching oil is required.

SMENOL WA CONC PASTE [13] Böhme

Used as a substitute for soap and degras for the fatting of vegetable tanned leather. Enhances fat take up and homogeneous distribution without an unfavorable action on water-proofness.

SMENOL WO CONC PASTE [8,13] Böhme

A yellowish paste. (See Cyclanon LA conc. paste). High molecular weight alcohol sulfonates. Properties: 50% sulfonates; acid no., 0; sap. no., 0; iodine no. (Hanus), 0; pH of 10% solution, 6.5–7.0; powerful emulsifier for fats, oils and waxes. Used alone or in combination with fat solution for the rubbing up of the grain.

SOFTENER ABG [10,11] I.G.F.

A viscous, liquid oil similar in solubility, composition and usage to Softener AG.

SOFTENER AG [10,11] I.G.F.

A solid, light-colored, wax-like product. Composed of esters more difficult to saponify than natural fats. Properties: m.p., 40-50°, insoluble in the usual fat solvents; soluble in alcohol. Used in impregnating leather. Leather thus treated is resistant to mechanical and chemical wear.

SOROMIN FL [10] I.G.F.

A water soluble, cation soap. Used to emulsify insoluble Derminol oils and natural fats. Especially suited as the emulsifying component of a soap-paste for greasing vegetable tanned leather.

SULTAFONOL B [15] Chem. Fabrik Stockhausen

Light-brown, clear oily liquid from which a white sediment separates on standing at room temperature. Properties: 59.6% volatile after 5 hrs. at 100°; 11.6% ash; 0.003% Fe_2O_3; no free strong acids or alkalies; pH of water extract, 6.52. Used as a fat-liquoring leather oil.

SUTRAMIN [8] J. Seidel, K. G. Grottau

Sulfonated mineral oil. Properties: 79% unsaponifiable material; pH of 5% emulsion, 4.9.

TALLOSAN SB CONC [15] Chem. Fabrik Stockhausen

Light colored salve-like mass. Properties: 34.7% volatile at 100°. after 5 hrs.; 8.8% ash; 0.003% Fe_2O_3; acid no., 13.5; pH of water extract, 7.48. Used as a supplementary greasing agent in greases especially for russet leather; increases water repellency. Can be used up to 50% of russet leather grease.

TANNOPOL M [8, 13] Chem. Fabrik Stockhausen

A viscous, dark-colored fluid. Properties: 44.4% volatile at 100°; 5.3% ash; pH of water extract, 6.36; water solution is clear blue and fluorescent. Recommended as an oil for vegetable tanned leather and for removing oil from vegetable tanned leather, either undiluted or dissolved 1:1 in water.

TRUPON 11/43 [8] CH. Trumpler, Chem. Fabr.

Composed of 34.3% riffette, 29.0% mineral oil and 22% exchange fat material. Properties: Fettzahl, 85.3. Gives finely dispersed emulsions suitable for preparation of liquors.

*UVM OIL [7, 11a]

Unreacted Mepasin, recovered after saponification of Mersol.

VORLAUFFETTSAURE ESTERS OF 2 I.G.F.

ETHYLHEXANE DIOL 1, 3 [22]

The esterification product of 2-ethylhexane-diol-1.3 with vorlauffettsaure (C_6-C_{10}). These fatty acids are the by-products of the edible fatty acid preparation from Fischer-Tropach paraffin.

WACHS 1501 [15] Böhme

Brown-colored, of hard salve-like consistency. Properties: 0.1% volatile after 5 hrs. at 100°; no mineral matter or harmful iron compounds; pH of water extract, 5.03. Can partly or completely replace tallow.

WAX OP [39] I.G.F.

Prepared from Montan Wax which has been oxidized with chromic acid, esterified with butylene glycol and saponified with $Ca(OH)_2$. This wax when mixed with spindle oil forms a good smearing agent for leather.

*WEICHHARZ XF [25] I.G.F.

A soft resin made by condensing xylol with formaldehyde. Used as an intermediate in the production of Derminol oil II and Corepale W. Also a similar high viscosity resin is used in the production of Corepale H. See Derminol oil (2).

Summary and Bibliography are found after No. IV of this series which follows.

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Synthetic Fat Replacement Materials for Leather

IV. THE PRINCIPAL I. G. FARBENINDUSTRIE EXCHANGE FATS

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EXCHANGE FATS DERIVED PRIMARILY FROM KOGASIN II.

The basic raw material from which several of the principal I. G. Farben exchange fats were derived was Kogasin II, a by-product of the synthetic liquid fuel industry, established in Germany in 1936. By 1940 the production of the synthetic fuel oil, Kogasin, was alleged to be over one million tons. Basically, it was produced by the catalytic hydrogenation of water gas, which was made by treating coke with steam at high temperatures. Kogasin II was the kerosenic fraction of Kogasin; one of its major uses was as a motor fuel.

(1)Chemistry of Kogasin [11a, 17, 21, 22, 23, 29, 40].

The French chemist, Sabatier, demonstrated in 1902 that carbon monoxide in the presence of nickel or iron as a catalyst can be hydrogenated to methane, according to the following reaction [41]: $CO + 3\ H_2 \longrightarrow CH_4 + H_2O$. In 1923 Fischer and Tropsch [42] reported a method of reducing CO in the presence of alkali-Fe catalysts at 400–450°C and at 100–150 atmospheres pressure. The product, called Synthol, proved to be a mixture of aliphatic alcohols, aldehydes, ketones, acids and esters. Few hydrocarbons were found in the mixture, but by heating Synthol at 450° for one hour a mixture of hydrocarbons was obtained. In 1926, Fischer and Tropsch [42] altered the condition of the reaction (lower pressure, high H/CO ratio, no alkali in catalyst) and obtained a product composed primarily of hydrocarbons, ranging from ethane to solid paraffin wax. In 1936 Fischer and Pichler [42] described the so-called middle-pressure synthesis by which at 0.5 to 0.15 atmospheres an optimum yield

of liquid and solid hydrocarbons was obtained; an important result was a prolongation of the life of the catalyst so that good yields were still obtained after 26 weeks of operation.

During the war two new syntheses were announced, "naphthene synthesis" and "iso-synthesis." The purpose of these developments was to produce an aviation gasoline of higher octane number. The "iso-synthesis" implied a direct production of iso-paraffins. For example, the C_4 fraction from this process contained 90 per cent iso-butane [42].

Kogasin was synthesized by adding hydrogen to water gas to approximate a H/CO ratio of 2/1, which was optimum with respect to reaction rate, maximum yield or product per cubic meter of raw gas (based on volume and time of contact) and "degree of conversion." [43] Before the gases were allowed to react they were freed from all sulfur by treatment first with iron oxide and finally with iron heated to 400°. The hydrogenation reaction was completed by passing the mixed gases over an iron, nickel or cobalt catalyst. Equations for the reaction follow:

$$nCO + 2nH_2 \longrightarrow CnH_{2n} + H_2O$$
$$nCO + (2n-1)H_2 \longrightarrow C_nH_{2n-2} + nH_2O$$

The main products of the reaction, as isolated by distillation, included motor fuel (Kogasin I), a gas oil (Diesel oil) fraction (Kogasin II), and a residue which was mainly a mixture of paraffin waxes. According to Tropsch and Koch [44], Kogasin I, i. e., the fraction boiling up to 220°, was a mixture of 65 per cent olefins, 0.1 per cent benzene, 0.4–0.5 per cent toluene, and the remainder paraffins. Kogasin I constituted about 60 per cent of the total Kogasin. Because of the predominantly straight chain character of the hydrocarbons of this fraction, the octane number was low; for the fraction boiling up to 150° (synthetic aviation gasoline) the octane number was 55 [41].

Kogasin II was composed of C_{10-15} chains; some reports stated C_{10-20}. It had a high cetane number (referring to ignition quality of the fuel, and the inverse of the octane number) due to the fact that the hydrocarbons were mainly straight chain. Kogasin II, upon analysis, gave a carbon content of 84.8 per cent and a hydrogen content of 15.2 per cent. From these analyses the average carbon chain for this material would be C_{14}; the empirical formula, $C_{14}H_{30}$; and a theoretical boiling point of 241° [45]. Analysis for olefins showed 5-11 per cent [45, 46]. Further analytical data were: [47]

Iodine number (Wi js)	4.6
Specific gravity	0.76
Flash point	120°F.
Pour point	–4°F.
Boiling index	420°F.
Cetane number	96

The wax fraction of Kogasin was similar to the paraffin wax fraction of petroleum and was similarly utilized. One use was in the production of synthetic fatty acids[5,31] which were made by catalytic oxidation of the wax. The resulting fatty acids, both odd and even carbon chains, were used in the manufacture of soap[18], cooking fat[5] and synthetic butter[5].

Kogasin wax was first distilled up to 450°. The distillates were separated by sweating and pressing into soft paraffin and slab paraffin, melting at 30-35° and 50-52° respectively[11a,29]. The residue at 450° melted at 90° and was undoubtedly the RB hard wax, mentioned later in this discussion. RB hard wax was either oxidized directly to give fatty acids or was chlorinated to 6-7 per cent chlorine content; the chlorinated wax was then pyrolized, and the resulting olefinic compounds oxidized to fatty acids.

A summary of the fractions obtained from Kogasin is found in Chart I.

(2) *The Mersols*[7,18,20,23,32,37,38] *and Immergan*

One of the most interesting exchange fats reported by the Schultz-Schubert leather team[6] was *Immergan*[2,6,7,10,11,13,36,36a], which could serve as a leather lubricant as well as an oil-tanning agent. Immergan was related to, and possibly identical with, one of the Mersols. The principal technological use for the Mersols was in the preparation of detergents which were soap substitutes[23].

The Mersols were made from Kogasin II by first hydrogenating it to remove olefinic materials. The hydrogenated Kogasin II was called *Mepasin*. *Mepasin* was, therefore, a mixture composed mainly of straight chain paraffinic hydrocarbons of C_{16-20} chain length. Mepasin was sulfochlorinated directly by passing through it a mixture of chlorine and sulfur dioxide in the presence of ultraviolet light by the famous Reed process[48]. As reported by Calcott[23], "The equipment in which the production of the alkyl sulfonyl chlorides was carried out consisted of 20 vertical steel towers, each approximately 20 feet high by 8 feet inside diameter; the bottom or reacting section of each of these containing 16 glass tubes 7 inches inside diameter running across the steel cylinder in the horizontal direction. In each of these tubes there were placed six 40–60 w. daylight lamps, i. e., the type which start on a tungsten filament and then operate as a mercury vapor light. In order to transmit as much ultraviolet light as practical, the glass tubes were made of 'normal glass.' The reaction section was 8 feet high. The entire steel cylinder and all pipe lines were lined with an acid resistant resin of the 'Haveg' type which lasts from six months to one year. The upper part of the reactor was filled rings of the same resin. In operating, Kogasin was circulated from the bottom of the reactor through a heat exchanger consisting of a water-cooled six inch pipe also lined with 'Haveg' and was returned to the top tower. Chlorine and sulfur dioxide were passed in at the bottom of the reactor and the hydrochloric acid, mixed with some excess sulfur dioxide, passed off at

the top. Circulation was brought about by means of a centrifugal pump with a porcelain impeller, and the valves were steel, lined with the 'Haveg'."

Mersol D was prepared as indicated above by reacting Mepasin with one mole each of the two gases. Under the conditions of the reaction the product consisted of approximately 50 per cent monosulfonyl chlorides, 30 per cent di-sulfonyl chlorides and 20 per cent unreacted Mepasin. Mersol D was for the most part shipped directly to the soap manufacturers, who saponified it to sodium sulfonates which were used as detergents. Use of larger amounts of the reacting gases was avoided because of the formation of larger amounts of the undesirable disulfonates.

As the war progressed, it became necessary to conserve the Mepasin lost in the production of Mersol D, and for this reason only one-half mole each of chlorine and sulfur dioxide was used in the chlorination. The product in this case was called Mersol H, and consisted of 50 per cent mono-sulfonyl chlorides and 50 per cent unreacted Mepasin; the latter could be recovered in large part by saponifying with soda and diluting the mixture, when the Mepasin separated, or by treatment of the mixture with liquid sulfur dioxide in which the Mepasin is insoluble (Edeleanu Process). The sodium sulfonates, made from Mersol H, foamed heavily in water and had excellent wetting properties [9].

A significant development for the leather industry was the use of the Mersols as an oil tanning material called Immergan. Immergan was a brownish, water-insoluble oil, with the following properties:

Viscosity (outflow at 20°)	16 secs.
Specific gravity	1.07
Ash	0
Volatility at 100°	11-12 per cent
Acid No.	20-50
Saponification No.	360-380

In the Schultz-Schubert report [7] it was stated that Immergan was made by fully sulfochlorinating Mepasin, which would make Immergan identical with Mersol D. There still remains some question whether the composition of Immergan was identical with that of Mersol D or Mersol H.

When Immergan was used as a tanning agent, limed and bated hides were usually subjected to a mild pre-tan with 0.5–2.0 per cent of 40 per cent formalin, pressed and then tanned with Immergan. As a rule, a 12 per cent Immergan solution was used with 2.5–3.0 per cent of soda ash in the vat. The tanned hides were hung in a warm spot for several days and washed with a large excess of warm water. More soda ash was added if necessary to prevent any oily residue.

The chemistry of Immergan tanning, or sulfonyl chloride tanning in general, is not definitely described in the several reports available but the

reaction seems to be a preferential one between the sulfonyl chloride group and the free amino or peptide linkages in the skin protein. Apparently, these active nitrogen groups react rapidly with the alkyl sulfonyl chloride in the presence of cold water, make alkaline with sodium carbonate. As a result of this chemical reaction a substituted sulfonamide is produced and the tanning oil is alleged to be fixed to the leather fiber.

Immergan tanned leather was used in Germany for gloves, riding boots, trouser trimmings, ornamental straps, etc.[10, 11]. The product produced a leather possessing all the properties of fish oil tanned chamois leather except for color and odor. The typical train oil-chamois color and odor could be obtained by finishing Immergan-chamois with a little train oil (fish oil) or degras. It was possible to tan cattle, sheep, pig, goat and small animal hides with Immergan. Reports have indicated that it had been used to some extent in heavy leather tannages (Cf. also, [36, 36a]).

Immergan finished chamois leather had the same tensile strength as train oil chamois, required less oiling time and did not desiccate in the air. Basic, neutral and acid colors were employed satisfactorily in the dyeing of Immergan chamois.

C. H. Roser Lederfabrik, A. F. Feuerbach-Stuttgart, manufactured leather for self-sealing fuel tanks. They thought that the product could be improved by using Immergan or Lickerol (Böhme) [6].

(3) *Derminolnarben Oil* [6, 7, 8, 10, 11, 15, 27, 22, 21]

Derminolnarben oil (Leather oil $^{1}/_{90}$) was the basic ingredient of three of I. G. Farben's principal exchange fats, namely Derminol fat 2, Dermino oil 1 and Derminollicker 1. Derminolnarben oil was made by chlorinating Kogasin II to a chlorine content of 39–40 per cent [7]. Thus, this oil was mainly a mixture of chlorinated paraffinic hydrocarbons. The introduction of chlorine into Kogasin II raised its viscosity to approximately that of neatsfoot and train oils; the resulting product was an excellent oiling agent for leather because of its easy penetration, but leathers, thus oiled, had little water repellency. However, various agents could be dissolved in Derminolnarben oil, imparting the desired water-repellency. German leather technologists discovered early that chlorinated hydrocarbons had greater affinity for the collagen of hides than simple hydrocarbons, such as mineral oil [26].

Derminolnarben oil was manufactured from either Kogasin II or UVM oil. UVM oil is unreacted Mepasin recovered after the saponification of Mersol [7]. The Kogasin II, or UVM oil, was dried by passing it over NaCl [7, 21]. The chlorine was introduced at 90–100° into a lead lined chlorinating vessel, approximately $^{3}/_{5}$ filled with porcelain rings. Measuring devices determined the rate of delivery of the Kogasin and the chlorine gas. Chlorination was considered to be complete (40 per cent) when a specific gravity of 1.08 (60°) was reached. The product was then stirred for one hour at 80° to remove HCl and then with potash for 6-7 hours to remove the last traces of this acid.

It was twice filter-pressed to give Derminolnarben oil. Analytical data[10] follow:

Fettzahl*	97	Avg. mol wt.	320–330
Sp. g. (20°)	1.12	Flame point	167
Acid No.	0	Burn point	192
Iodine No.	1.0	Viscosity 20°	30–35 secs.**
pH	5.7	Viscosity 54.4°	92.5 S.U.S.***

* Per cent residue upon heating 5 hrs. at 95-100°.
** Fordbeaker, 4 mm. tip
*** Determined on an authentic specimen in our laboratory.

Since Kogasin II is mainly a mixture of C_{16-20} paraffinic hydrocarbons, the principal reaction during chlorination is substitution, one-half of the chlorine appearing in the oil and the other half as HCl. However, Kogasin II contained varying amounts (11-28 per cent) of olefins, which would add chlorine by 1-2 addition. The following data indicate the degree of chlorination in relation to specific gravity.

Degree of Chlorination	Increase in Wt. per cent	Cl per cent	Sp. g. 20°
Kogasin II.....	0	0	0.774
Monochloro-Kogasin.....	17.4	14.8	0.872
Dichloro-Kogasin.....	34.8	25.8	0.977
Trichloro-Kogasin	52.2	34.3	1.057
Tetrachloro-Kogasin	69.5	41.0	1.139
Hexachloro-Kogasin	104.3	51.0	1.292

Chlorination beyond the hexachloro-state is difficult, higher temperatures being required. From the data above, and considering the average molecule to be C_{18}, it is clear that the average chlorinated hydrocarbon in Derminolnarben oil is tetrachloropentadecane. Because of the complexity of composition of Kogasin II and since chlorine introduction is essentially random, it follows that Derminolnarben oil is an extremely complex mixture of chlorinated hydrocarbons. This probably accounts for the smooth properties of the oil. We could obtain no precipitation from this oil, even when cooled to - 75°

The central importance of Derminolnarben oil as an exchange fat makes the question of its stability a highly significant one. This is especially so because of the unsavory reputation of chlorinated hydrocarbons in this country with respect to their tendency to release HCl under practical use conditions[19]. From various individuals who were consulted on this question we were given to understand that branched chain hydrocarbons and the naphthenes, when chlorinated, would give products which are especially

unstable, because of the possibility of the presence of chlorine atoms on tertiary carbon atoms.

Kogasin II was known to contain considerable amounts of branched chain and naphthenic compounds; some of these are mentioned in connection with possible toxic effects of synthetic fatty acids made from them and designed for and used as food fats. Even the chlorinated normal paraffins, the main constituents of Kogasin II, slowly liberated HCl in the presence of oxygen, ultraviolet light, moisture and catalysts such as iron and copper. These factors were known to favor instability. On the other hand, chlorinated normal paraffins could be stabilized against light [50] by the use of selected filters. Decomposition retardents mentioned in the Schultz-Schubert report [7] included:

Magnesium carbonate
Lead carbonate
Litharge
Potassium nitrate
Aluminum stearate
Barium phthalimide
Lead linoleate
Dicyandiamine
Lecithin
Amines

Obviously, many of these materials simply acted by neutralization of the HCl as formed; this action was especially important because of the autocatalytic effect of HCl on the reaction. Other retardants are triethanolamine and epichlorhydrin. Incidentally, our work has resulted in preparing Derminolnarben oil analogues which are considerably more stable than the German product, mainly because of the practically complete absence of branched chain and naphthenic compounds in the hydrocarbon mixture from which they were prepared.

(4) *Derminol Fats* 1 *and* 2

Derminol fat 1 [8,9,12,27,26,11,11a] was a chlorinated hard wax of 12–13 per cent chlorine content. It seems to have been made from RB hard wax of S. P. 90–95°. Its properties were as follows: m. p. 42-3°; Fettzahl, 94; acid no. 0.5; iodine no., 0.3; pH of water extract, 5.0. It was designed for use in greasing vegetable tanned upper leather. It could be substituted for tallow up to 50 per cent. However, because of its high molecular weight its use as a tallow substitute was not entirely satisfactory. Before the end of the war its use in leather was largely superseded by Derminol fat 2.

Derminol fat 2 [7,8,9,10,15,22,29,11,11a] was a mixture of about 70 parts of Derminolnarben oil with 30 parts of a chlorinated RB hard wax [4,7,19]. The wax was a high melting paraffinic fraction from Kogasin of solidification

point 90-95°. It was chlorinated at 100° to 6-7 per cent chlorine content. It is to be noted that this chlorinated hard wax was designed originally as a means of introducing functional groups into the wax in order more easily to prepare synthetic fatty acids. By pyrolysis, chlorine could be driven off as HCl and the resulting olefinic compounds could be oxidized to fatty acids. The use of the chlorinated hard wax in a leather exchange fat is thought to be secondary to the original purpose of the material. A mixture of this material with Derminolnarben oil was superior as a greasing agent in leather to Derminol fat 1, probably because the Derminolnarben oil provided easy penetration, and the wax water resistance.

The several production sheets and reports do not state the exact composition of the Derminolnarben oil-chlorinated hard wax mixture. We found in the course of this investigation that the 70–30 mixture was about right to give a product of tallow consistency. Obviously, the proportions of the two components can be adjusted to give a product of any consistency within the limits of the two ingredients.

Progressive introduction of chlorine into a hard wax, according to our experience, rapidly lowers the melting point. A wax containing 25 per cent chlorine, for example, is a thick viscous liquid which will pour at room temperature. With 12 per cent chlorine the wax is like soft beeswax.

Derminol fat 2 is a light, yellow-brown paste of the consistency of a soft tallow. It is readily soluble in the common fat solvents and miscible in all proportions with natural fats and the Derminols. Analytical data reported for this exchange fat follow:[9,10]

Specific g. (20°)	1.022
Flow point	55°
Drip point	56°
Fettzahl	97.2
Acid no.	1.0
Iodine no. (Hanus)	4.5
pH of water extract	5.5

Derminol fat 2 was alleged to react with any metal with which it came in contact if heated for any length of time at temperatures above 100°. Derminol fat 2 was used in fat liquors and in greasing military uppers, smooth leather and harness and strap leathers. It was readily taken up by leather and imparted water repellency to about the same extent as tallow, but somewhat less than the corresponding fast acting degras. It could be blended with oils without the leather losing its water-repellent properties or becoming too soft. It was reported to impart fullness to the leather, good color, feel, tensile strength and porosity[10].

(5) *Derminol Oil* 1. [7,8,9,10,27,11,11a]

One method, devised by I. G. Farben to increase the water repellency of Derminolnarben oil, was to incorporate into it considerable amounts of

Igevin J30, a liquid but very viscous, sticky polymer of vinyl isobutyl ether, the resulting product being called Derminol oil 1 (DO-1). DO-1 was a mixture of approximately three parts of Derminolnarben oil and one part of Igevin J30. The chemistry of the Igevins and related products, the Densodrins, is discussed later in this report. Naturally the addition of the Igevin increases the viscosity of the Derminolnarben oil.

In practice the oil was made by mixing the Derminolnarben oil, warmed to 30–35°, with the Igevin, heated to 40–60°, in a warming cabinet. Actually, the final composition of the product was so adjusted that the resulting viscosity was 80–100 seconds, as measured in a Fordbeaker cup with 4mm. tip at 20°.

No authentic specimen of Igevin J30 was available for study in the course of developing this problem. However, similar material, synthesized in this laboratory, was found to be quite temperamental in relation to its compatibility with the Derminolnarben oil. Some of our DO-1 analogues tended to separate into two layers when cooled below room temperature. With Derminolnarben oil, made from Ultrax 20, for example, it was necessary to keep the chlorine content of the Ultrax below 30 per cent to retain compatibility at lower temperature.

DO-1 was slightly brownish yellow in color. Analytical data on the oil follow:[10]

Fettzahl	96
Ash	0
Sp. g. 20°	1.06
Acid no.	0
Iodine no.	3.1
pH of water extract	6.5

DO-1 was the most important replacement fat for cod oil and was manufactured in large amounts. It was used to fat-liquor russet and harness leather, vegetable tanned upper leather and case and strap leathers. It was unsaponifiable. While its viscosity was similar to that of train oil and it possessed certain other similar properties in leather processing, it contained no highly unsaturated compounds as does train oil. It penetrated leather well, distributed uniformly, counteracted mildew growth and produced a leather which was water repellent, tough and flexible. It was a good natural fat solvent, mixing with the natural fats in all proportions. Leather treated with this oil did not change in fat content over a number of years. In a report by Dr. Otto[26] the following statement was made: "By experiment on the polyvinyl ethers, it was established that by oxidation one mole of oxygen is taken up and that, then, after the primary formation of peroxides on the ether oxygen, cross linking of the polyvinyl ether chains, which probably takes place over the oxygen bridge, automatically occurs." He further stated: "since about the middle of 1940, polyvinyl ether, carried under the designa-

tion *Leather Oil* 1239 in the trade, is to be looked upon as a fully equivalent exchange product for train oil."

Schultz and Schubert[6] reported several specific examples of the use of DO-1 by German Tanners. J. Mayer and Son used this exchange fat, soap and 0.5 per cent of neatsfoot oil for upper leathers. They preferred DO-1 to natural oils. On the other hand the Ludw. Lindgens K. G. Lederfabrik considered the synthetic lipid better than poor cod oil, and preferred to use mixtures of the synthetic and natural oils. Lederwerke Becker used DO-1, Derminol degras and Derminol fat 2 in equal parts for fat-liquoring. They liked the products because a better color was obtained by the use of these fatting agents, but they were not certain how well the leather would stand aging. The Carl Freudenberg Company employed a mixture of DO-1, Derminol fat 2, degras and tallow and obtained as satisfactory results as with natural fats and oils. The A. Hodom Lederfabrik plant used DO-1, but preferred the natural oils such as neatsfoot; they maintained that the synthetic products produced a "drier and hungrier" feel. The Carl Kaess Lederfabrik Company used a mixture of exchange fats and tallow. Lederwerke Weimann of Neumuenster used DO-1, fat and tallow and preferred cod oil moellon and tallow. They claimed it was necessary to have some natural fats with the substitutes in order to achieve the proper feel. Fr. Vogel Matteghofen of Austria claimed that Derminolnarben oil, Derminol fat 2 and degras were as good as nautral fats, but they preferred the latter. They stated further that their associates, Herschberg Saale, preferred the exchange fats. A Czechoslovakian leather company, Trantisek Policky Jaremer, used 30–40 per cent DO-1 and fats and liked them.

(6) *Derminollicker* 1. [7,8,9,10,13,27,22,18,11,11a]

Derminollicker 1 (DL-1) was a fat-liquor replacement material of unique composition; it was designed to replace neatsfoot and cod oils and the corresponding sulfated oils. Chemically, it was a water-miscible mixture (or solution) of Derminolnarben oil, unreacted Mepasin (UVM oil) and the sulfonamides and amido-acetic acids derived from Mepasin[7]. The hydrophilic components, or emulsifying agents, of the mixture were the amides and amido-acids, known as Amide H and Acid H. These were made from Mersol H by amidizing with liquid ammonia, which formed the Mersol sulfamide; this amide was then converted into the potassium salt with KOH and was reacted with sodium chloroacetate to give the sodium salt of Acid H. Another name for the Sodium Sulfamido acetate was Emulphor STH, or STX. The former contained 50% unreacted Mepasin, the latter 30%[30]. Since Mersol H contained approximately 50 per cent of unreacted Mepasin, both the amide and acid, derived from Mersol H, contained this same amount of Mepasin so that in the composition noted below the unreacted Mepasin was probably added fortuitously with the emulsifying agents rather than intentionally.

It is difficult to see what desirable property could be imparted by this hydrocarbon. The synthesis of these materials is described in the following chart, again assuming pentadecane to be the average hydrocarbon present.

$$C_{15}H_{32} \xrightarrow[Cl_2]{SO_2} \underset{\text{Mersol H}}{C_{15}H_{31}SO_2Cl} \xrightarrow{NH_3} \underset{\text{Amide H}}{C_{15}H_{31}SO_2NH_2} \xrightarrow{KOH} C_{15}H_{31}SO_2NHK \xrightarrow[ClCH_2\text{-}COONa]{} \underset{\text{Acid H sodium salt.}}{C_{15}H_{31}SO_2NH\text{-}CH_2\text{-}COONa}$$

The alleged composition of DL-1 was as follows:

Derminolnarben oil	25 per cent
Unreacted Mepasin	28 per cent
Amide-H	7 per cent
Acid H	20 per cent
Water	20 per cent

DL-1 was a bright yellow to brownish, viscous oil, which could be diluted with water in all proportions to form a clear solution. Analytical data follow:

Specific gravity	0.981
Fettzahl	67
Ash, per cent	2.6
Saponification number	45
Acid no.	21
pH of 10% water soln	5.8

Usually DL-1 was not employed alone on mineral tanned leathers, but was used alone with some other oil such as DO-1. In vegetable tannages it was immaterial whether water-insoluble oil was added or not. Different oiling effects were obtained by oiling with DL-1 along with water soluble or water insoluble oils; hence, the more DO-1 added to the mixture, the more filled and pliable the leather. If the mixture was not allowed to stand too long (preferably used on the day of mixing), as much as two parts of DO-1 in one part of DL-1 could be formulated satisfactorily [10].

When a DL-1-fat mixture was used in oiling leather, a uniform distribution of the fat on the leather was obtained similar to the results with sulfated oils. Since DL-1 imparted no great absorptive power to the leather, as did the sulfated oils, the leather could be tanned in the usual manner. Since the liquor was very resistant to light and did not turn the leather yellow, it was particularly adapted to use in oiling light colored and white leathers. It was resistant to cold and not sensitive to metals except on long contact at

high temperatures. The emulsions dispersed with DL-1 were indifferent to the addition of acids and salts. If the licker separated or became turbid on long standing, it could be restored to its original state by heating 100 kg. of the licker with 0.5 to 1.0 kg. of technical grade ammonia. It was used for fat-liquoring horse hide stocks and fronts, and calf skin uppers[10].

The unique chemical features of DL-1 are its Amide H and Acid H components which serve as emulsifying agents. Whether these materials possess special virtues as fat-liquoring adjuncts is open to question. It should be noted again that these materials are sulfonamides and sulfamido-acetic acids. It is possible, therefore, that their similarity to the peptide linkages of the proteins may cause them to have unusual chemical affinity for the leather proteins. On the other hand, we are of the opinion that these materials were used simply because they were available in connection with other uses of Mersol in the preparation of soap substitutes, rather than because of special virtues in leather.

Exchange Fats Derived from Miscellaneous Sources

(1) *Derminol Oil* 2. [7,8,9,10,13,27,26,25,11,11a]

Derminol oil 2 (DO-2) was a unique exchange oil, made by condensing a xylene formaldehyde soft resin (Weichharz XF)[25] with a mixture of C_{9-10} alcohols. The Production Sheets, included in the S. and S. report [7], gave the following description of the actual synthesis of this oil: 1500 kilograms of Weichharz soft resin (standardized to 10.3 per cent oxygen) was mixed with 1200 kg. of Læuna alcohol (boiling 180-220°) with stirring and, after the addition of 45 kg. of Fuller's earth, the mixture was heated to 130-170°. During the process 90 kg. of water was given off. The condensation was finished in 4-6 hours. The Fuller's earth was filtered off and the unreacted alcohol was removed by vacuum distillation. The yield of DO-2 was about 1950 kg.

DO-2 was a light yellow-brown, clear oil, containing no crystallizable constituents. It was neutral and unsaponifiable and was alleged to be capable of absorbing oxygen. In our experience, however, its drying capacity was very low. The oil was easily soluble in carbon tetrachloride, ether and benzene, and somewhat less soluble in petroleum ether. It was less readily emulsifiable than DO-1. DO-2 did not corrode metals. It did not irritate the skin. It was free of iron, acid, alkali and other compounds which might be harmful to leather. Analytical data on the oil follow:[10]

Specific gravity (20°)	0.992
Fettzahl	93.3
Ash	0
Ash no.	0.8
Iodine no.	6.4
pH of water extract	4.9

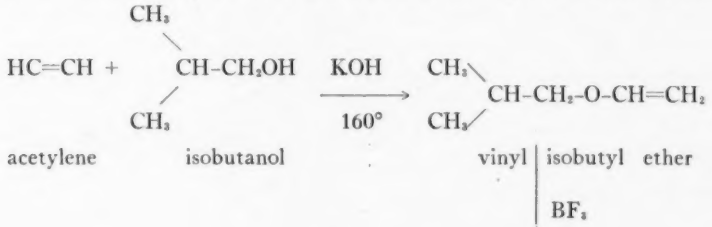
DO-2 was not affected by enzyme action, was easily absorbed by leather and inhibited mold formation. Leather, fat-liquored with this oil, was soft and flexible and had a texture similar to that of leather finished with train oil or DO-1.

DO-2 was a substitute for train and neatsfoot oils. In one report [26] mention is made of a Leather oil Le 265 which is apparently identical with DO-2. The drying and water-proofing properties of the oil are noted in this report.

(2) *The Igevins and Densodrins.* [7, 8, 9, 33, 26, 34, 35, 19, 11a]

The Igevins have already been mentioned in describing Derminol oil 1. Igevin J30 and Densodrin NW are extremely viscous liquids, polymers of vinyl isobutyl ether. Densodrin NH is a resin similar to colophony and was made from B-decalol vinyl ether [7]. Because of the general importance of these polymers not only in leather but also in other textiles, we will include in this section of our report first their special technology and applications in leather, and then a more general description of the Igevins and Densodrins for other uses. We feel that some of these polymers may become useful in imparting water resistance to leather when they are incorporated in such exchange fats as Derminol fat 2 and Derminolnarben oil.

The following description of the process of manufacture of Densodrin NW was taken from notes made available to us by Adolph Schubert [36]. "100 liters of purified vinyl isobutyl ether was run into a polymerization vessel at about 80°, i. e., the boiling point of the ether. 500-600 cc. of catalyst (0.5 per cent solution of boron trifluoride dihydrate in dioxane) was added in 20 minutes with stirring. The start of the reaction was marked by a sudden rise in temperature, accompanied by rapid refluxing. When the temperature had reached 90°, further vinyl isobutyl ether was added continuously at the rate of 280 liters per minute; simultaneously, 800 cc. of catalyst was added per hour. Within one hour a temperature of 120° was reached. At a temperature of 125° (25 hours) the process was carried on continuously, the temperature being maintained by running cold water over the reaction vessel. From the polymerization vessel the product was drawn off and stored in barrels. The yield was about 98 per cent". The synthesis, starting with acetylene, follows:



Densodrin NH was prepared by a similar procedure, starting with B-decalol (hydrogenated Beta-naphthol). This solid resin softened at 65-75°.

We had at our disposal for examination small specimens of Densodrins NW and NH but no Igevin J30. However, the Densodrin NW apparently differed from the Igevin only in k-value, this being about ten points lower for the Densodrin.

Igevin J30, as synthesized in our laboratory, was an extremely viscous, sticky, light amber liquid which mixed readily with authentic Derminolnarben oil. As stated previously, when the Derminolnarben oil was made from Ultrax 20 wax, it was necessary to keep the chlorine content of the wax below 30 per cent. Otherwise, separation occurred at low temperatures.

The k-value used by the I. G. Farbenindustrie in characterizing their polymers is based upon the equation devised by Fickentscher and Mark [50, 51]

$$\frac{\text{Natural log } (N_s/N_o)}{c} = \frac{75\,k^2}{1 + 1.5\,kc.} + k, \text{ where}$$

N_s=Kinematic viscosity of the polymer solution
N_o=viscosity of solvent
c= concentration of polymer in grams per cc. solution
k = a parameter characteristic of the polymer.

It was stated that the k-value, multiplied by 1,000, gave a rough estimate of the molecular weight of the polymer. Thus, the average particle size in Igevin J30 would be about 30,000. It is important in stating the k-value to note whether natural or base-10 logarithms are used in solving the equation. We found the Igevin J30 analogue synthesized at Ohio State University to have a k-value of 28, when calculated using natural logarithms, corresponding, as we supposed, with the German product J30 but the k-value was 18 calculated with base-10 logarithms.

The Igevins and the Densodrins were unsaponifiable. The latter could be applied directly to leather in 20–30 per cent solution in carbon tetrachloride or wash benzine. The leather to be thus impregnated was placed in the solution until all of the air was displaced, and then was removed and allowed to air dry. The Densodrins were said to loosen the fibers and penetrate uniformly into the leather. After evaporation of the solvent, a uniform resin film was left on the surface [7]. We believe the best use of the Igevins and Densodrins is to apply them in solution with some penetrating oil such as Derminolnarben oil. Their use in this form has been shown to be practical by tests at the University of Cincinnati [3].

(3) *Further Description of the Igevins and Densodrins.*

As noted previously, Igevin J30, an important constituent of DO-1 was a polymer of vinyl isobutyl ether. The production of the monomer was based on the synthesis developed by Reppe [50, 52]. His first vinylations were carried

out in 1928[50] by reaction of vinyl chloride and sodium alcoholate. In 1930 he took out patents for the preparation of vinyl alkyl ethers from acetylene and alcohols under relatively high pressures with alkaline catalysts (sodium, potassium, potassium hydroxide, alcoholates, phenates, cyanides) and also the zinc and cadmium salts of organic acids[53]. In addition to vinyl isobutyl ether, the Germans produced polymers of vinyl methyl ether, vinyl ethyl ether, vinyl beta-decalol ether, vinyl octadecyl ether and vinyl ethers of hydrogenated sperm oil, of cocanut oil, of tall oil ether and some divinyl ethers. These are described in Table 1.

TABLE 1

Composition and Properties of Igevins and Densodrins*

Polymer	Composition	Characteristics
Igevin A 25*	Polyvinyl ethyl ether	Thick liquid. Soft resin. Both sol. in methanol; low mol. wt. types, sol. in benzol; not completely water-sol.
Igevin A 50*	Polyvinyl ethyl ether	
Igevin AZ 28	Copoly-(20 vinyl ethyl ether) mer (80 vinyl decalol ether)	.....
Igevin D and DJ		Hard wax; Soft pts: D,70-75°; DJ, 65-70°.
Igevin M 40	Polyvinyl methyl ether	Very viscous, soft resin, sol. in water and ethanol; insol. in benzene.
Appretan WL	Aqueous sol'n Igevin M 40	.....
Plastomoll SW	70% Igevin M in Methyl Acetate	.....
Igevin J (or I) 20**	Polyvinyl isobutyl ether	Viscous liquid
Igevin J 30**	Polyvinyl isobutyl ether	Viscous liquid
Igevin J 60**	Polyvinyl isobutyl ether	Very viscous soft resin
Oppanol C	K-value 100-130, Mol. Wt. 150,000	Soft resin, benzene sol.; insol. in ethanol, water.
Igevin Z	Polyvinyl betadecalol ether	Hard resin; sol. in benzene, toluene; insol. in ethanol, water.
Igevin ZI(ZJ)	Copolymer 60% Igevin Z 40% Igevin I	.....
Igevin ZJR	Copolymer 20 vinyl isobutyl ether 80 vinyl decalol ether	.....

Polymer	Composition	Characteristics
Densodrin H	Polyvinyl ether of hydrogenated sperm oil plus 30% resin	.....
Densodrin NH	Polyvinyl Beta-decalol ether	Solid resin
Densodrin W	Copolymer 80 vinyl ether of hydrogenated sperm oil 20 vinyl ether of cocoanut oil.	.....
Densodrin V	Polyvinyl ether of hydrogenated sperm oil	
Densodrin NW	Polyvinyl isobutyl ether: k-value 14.	Viscous liquid
Densodrin AW	.....	.....
I G Wachs	Polyvinyl octadecyl ether	.....
Bindemittel Li 10	Copolymer vinyl methyl ether, 66 divinyl diglycol ether, 5.5 vinyl tall oil ether, 28.5	

* Data above are taken from (39, 33, 50, 54, 7, 55).
** Numerals indicated molecular weight in thousands.

These polymers found various applications as adhesives, impregnating agents and lacquer constituents. A wide range of solubilities and compatibilities, as evidenced in Table II, gave raise to extensive uses.

The Igevins were stable to light, highly resistant to saponifying agents, and had excellent adhesive powers on bases of all kinds. Irevin M 40 possessed the unusual property of water and organic solvent solubility. This feature could be utilized in cementing materials on wet undergounds, such as flesh hides [33]. Addition of the Igevins to film components or impregnation with these substances improved the adhesive quality and pliability of the film of material [33, 50]. Thus we find them as components of adhesives for pasting textiles on leather, wood, metal, glass, for plastic coatings of the heat sensitive type, preparation of shoe bottom filler, waterproof paper sacks and cartons, and fly and insect protecting resins. Igevins D and DJ imparted film fastness and heat resistance. The oil resistant properties were utilized for coatings of oil bottles and oil resistant cables [33]. In trade they appeared in solutions of benzene, acetone or esters under the name of Cosals. As copoly-

TABLE II

Solubilities of the Igevins

Solvent	M 40	A 50	A 25	J 60	J 30	J 20	D J	D
Water	+*	0	0*	0	0	0	0	0
Methanol	+	+	+	0	0	0	0	0
Ethanol	+	+	+	0	0	0	0	0
Acetone	+	+	+	0	+	+	0	0
Diethyl Ether	+	+	+	+	+	+	+	+
Ethyl Acetate	+	+	+	+	+	+	0	0
Penzene	+	+	+	+	+	+	+	+
Toluene	+	+	+	+	+	+	+	+
Xylene	+	+	+	+	+	+	+	+
Petrol	0	+	+	+	+	+	+	+
Methylene Chloride	+	+	+	+	+	+	+	+
Chloroform	+	+	+	+	+	+	+	+
Carbon Tetrachloride	+	+	+	+	+	+	+	+
Trichloroethylene	+	+	+	+	+	+	+	+

* —Clearly soluble; 0 Insoluble

mers with acrylic esters they were known as Acronals [50]. The largest field was that of long-time contact adhesives such as scotch and adhesive tapes.

The Densodrins were non-saponifiable. Their application was limited more to the *leather field*. They improved the wear and tear resistance and water resistance of leather [10, 85]. Admixture of the Densodrins with fat-liquoring agents improves the action of the latter.

Exchange Fats of Unknown Composition

(1) *Derminol oil* 3 [10, 11, 11a]

No exact information is available as to the chemical nature of this oil. It was stated to be a high molecular weight aromatic ester developed as a substitute for train oil and animal and vegetable fats. It was a delicate yellow in color, was soluble in the common fat solvents and miscible in all proportions with the natural and synthetic fats. Its viscosity was similar to that of train oil. It did not attack metals and was not changed by enzyme action. Derminol oil 3 emulsified well and worked as the unsulfated component of the liquor mixture. It had a marked affinity for leather fibers, distributed uniformly in leather, and imparted a uniform light color and tough qualities to the leather. It inhibited mildew formation. Analytical data on the oil follow:

Specific gravity 20°	1.085
Fettzahl	96
Ash per cent	0.42
Acid no.	0.4
Saponification no.	135
pH of water extract	4.75

(2) *Derminol Degras* 1. [10,11,11a]

Derminol degras 1, developed as an exchange material for degras, was a "select mixture of esters chemically similar to natural fats," which contain oxygen rich groups. It was an ochre-yellow paste of salve-like consistency, was readily soluble in the common fat solvents, and was compatible with synthetic and natural fats. It could not be heated above 80° since loss of moisture prevented its becoming uniformly distributed in leather. Derminol degras 1 worked well on wet leather and imparted water-repellency to leather, like natural degras. It did not corrode metals. It possessed many advantages over natural degras in the oiling of mineral tanned leather. Analytical data follow:

Specific gravity	0.986
Fettzahl	76
Ash, per cent	1.0
Acid no.	26.0
Iodine no.	47
Saponification no.	90
pH of water extract	4.6

(3) *Derminolliker* P.

This licker [10,11] was developed as a substitute for the natural fats for use in the treatment of pelts. Its composition was so devised as to make it compatible with mineral tanning agents and salts in high concentrations, and, because of its high electrolyte stability, it was especially applicable in oiling pelts. Derminollicker P was a dark brown viscous oil, miscible in all proportions in water. It penetrated the skin quickly and produced a soft and flexible leather. It could be used alone or with natural and synthetic fat materials. Analytical data follow:

Specific gravity	0.894
Fettzahl	85
Ash, per cent	0.02
Saponification no.	36
pH, diluted with 9 parts water	7.02

Chart Summarizing the Chemistry of the Principal I. G. Farben Exchange Fats

The chemistry of the principal I. G. Farben exchange fats, described above, of which the chemical nature is definitely known, is summarized in Chart 1.

It is to be noted that the charts in Leather Series Report No. 3, issued by O.T.S., [11a] were taken from one of the earlier editions of Chart 1.

Formulations for the Application of Exchange Fats

The formulations included below are selected from a large series which are found in Leather Series Reports Nos. 3 and 4 [11,11a].

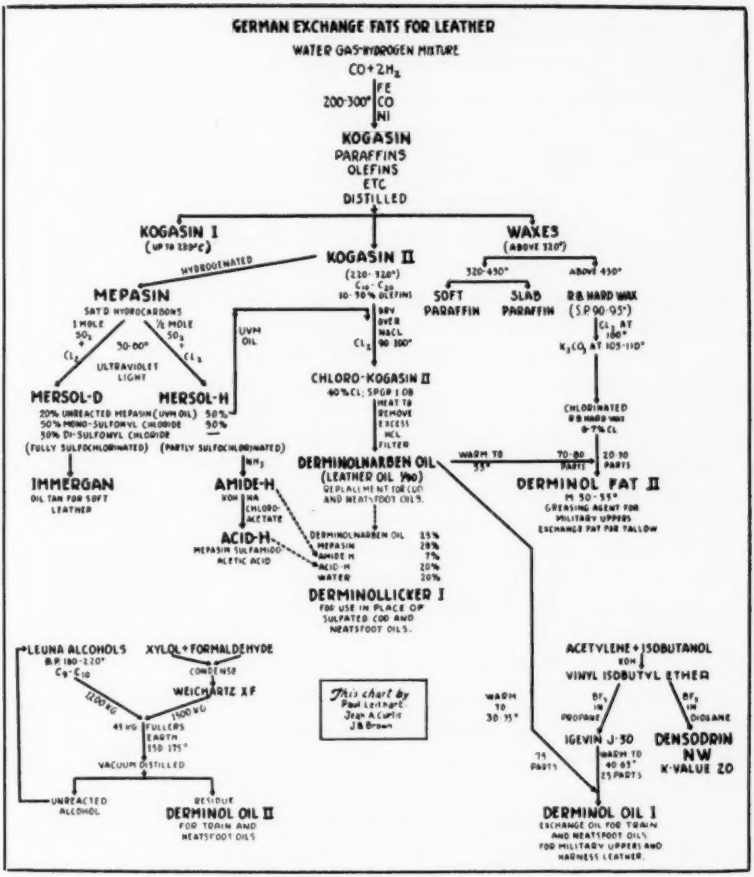


CHART I

(1) *Densodrin Formulation*

For upper leather the following are used: 50-100 grams of Densodrin NW is dissolved in one liter of carbon tetrachloride, wash benzine or a mixture of both solvents. The leather is soaked 10–20 seconds in this solvent and then dried in the air. Greased upper leather is impregnated by repeatedly applying this solution to the leather surface in order to avoid dissolving out the fat.

(2) *Derminol Formulations for Leather Treatment.*

The Germans had various quantities of beef tallow and degras available; hence, the I. G. Farbenindustrie recommended the following mixtures:

(a) Stuffing agents for vegetable tanned military upper leather:

15	parts	Derminol fat 2
20	"	Beef tallow
50	"	Derminol oil 1
15	"	Degras
100	parts	

The solid constituents are melted in a kettle, in the order stated above. The Derminol oil is slowly added and, finally the degras is stirred into the melt. This mixture had a Fettzahl of 94.4 (assuming a standard degras was used with Fettzahl of 75). It was taken up uniformly by leather; it was a good water repellent without injuring the porosity to any degree. Derminol degras 1 could be used to advantage in the mixture; it increased the tensile strength of the leather. The Fettzahl remained the same.

(b) The following mixture contained no beef tallow:

33	parts	Derminol fat 2
10	"	solid mineral wax or oil, ceresin or vaseline
43	"	Derminol oil 1
14	"	Degras
100	parts	

The constituents were put in a melting kettle in the specified order, and the degras stirred in last without further heating. Depending on the consistency of the mineral oil ingredient this mixture made the leather more or less firm.

(c) The folowing was a mixture containing only exchange fats; also used for military uppers:

30	parts	Derminol fat 2
60	"	Derminol oil 1
10	"	Derminol degras 1
100	Parts	

The Derminol fat 2 is melted, the Derminol oil 1 slowly added and, after removal of the moisture and lowering the temperature of the mass below 80°, the Derminol degras 1 is added. This mixture has a Fettzahl of 94. It is absorbed readily and uniformly by the leather and confers all of the desired characteristics.

(d) Fat liquor for smooth leather

The following mixture could be used for drum or vat greasing:

20	parts	Derminol fat 2
32	"	tallow
40	"	Derminol oil 1
8	"	Derminollicker 1
100	parts	Fettzahl 96

The Derminol fat is melted with the tallow. The Derminol oil 1 and Derminollicker are then stirred into the mix in that order. This fat-liquor is uniformly taken up and makes the leather tough and resistant.

Summary

In this and the preceding paper of this series we have described the origin, objectives and purposes of an extended investigation of German fat replacement materials for leather. A Glossary of exchange fats was presented, giving names of products, manufacturers, and physical and chemical properties of large series of materials which were proposed as suitable products for oiling, greasing and fat-liquoring leather. Following this, the principal I. G. Farbenindustrie exchange fats were described in detail and several actual formulations were described for introducing these materials into leather. In reports to follow we propose to describe the synthesis of analogues of a number of these exchange fats from raw materials available in American industry.

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Received June 3, 1951

ABSTRACTS

Fellmongering Investigations XVI. Survey of the Bacterial Flora of Sheepskins. By M. E. Maxwell. *Australian J. Applied Sci.*, **I,** 497 (1950). Forty-two samples of sheepskin and wool from U. S. A., Canada, and Britain have been examined bacteriologically and the results compared with those obtained with Australian skins. Eighty-three species of aerobic bacteria have been isolated and their biochemical reactions studied. On dry skins the genera of bacteria are the same as on Australian sheepskins, although the species within these genera vary with the locality from which the sheepskin is obtained. The predominant bacterium on the wool roots from all skins from United States of America and Canada at the termination of sweating is a species of *Pseudomonas*. These skin samples all require 3-8 days at 25°C. for complete wool loosening. The two samples of dry skin from Britain show the same predominant flora as the Australian skins at the termination of sweating, namely, a strain of *Proteus vulgaris* and a species of Achromobacter.

Fellmongering Investigations XV. Recovery of Wool from Skin Pieces by Water Digestion Methods. By T. A. Pressley. *Australian, J. Applied Sci.*, **I,** 484 (1950). The usual method of recovering wool from sheepskin pieces employs complete digestion of the skin tissues by immersion in water. An investigation of this method was made using pieces of dried crossbred skin, soaked back and thermally shrunk prior to digestion. Digestion is most active at 35 to 40°C., and takes place in a series of stages; an initial lag phase is followed by a phase of rapid digestion, then by a retardation phase during which the rate of digestion becomes progressively slower until complete. Delimed painted pieces are digested very slowly, but sweated pieces are rapidly attacked. Indeed, much nitrogenous material is brought into solution even during the thermal shrinkage of sweated skin, and the course of digestion is unlike that of unsweated skin. Of the methods tested for acceler-

ating digestion, two warrant full-scale trials; (a) sweating the pieces prior to shrinkage, and (b) immersion after shrinkage for approximately 8 hours in mold bran extract rich in proteolytic enzymes. The mold extract is then replaced by water and used for a further batch of pieces. This method appears to offer special scope for dealing with delimed painted pieces. The wool recovered by water digestion methods is of good quality, provided the water is changed frequently. The unpleasant odor of the recovered wool is largely removed by treatment with a hot, dilute solution of soda ash.

Contribution to the Study of Rapid Tannage. By H. Comte et M. Mercier. (Conference No. 4 *Association Francaise des Chimistes des Industries Du Cuir*—20 Janiver 1949). The authors describe a rapid vegetable tanning process for sole leather using a chestnut extract specially manufactured for this purpose and having pH = 4.2, absence of mineral matter, and a very high tannin/non-tannin ratio. The penetration of this extract is as rapid as that of cold soluble quebracho but the fixation of tannin in the hide is greater. Works experiments have been carried out using 8 suspenders with liquors from 1° to 8° Bé, heated to temperatures ranging from 15° to 32°C. The ratio of weight of hides to volume of liquor was 6 in all pits. Addition of extract was made only to the head liquor. The method of running of the liquor from each pit enabled considerable amounts of liquor, perfectly exhausted in tannin, to be run to waste. In this way, it was possible to avoid accumulation of non-tannins in the liquors and a high fixation of tannin was obtained in the hide. The hides remained 3 days in each pit, giving a total tanning time of 4 weeks.

The suspenders were followed by two retanning processes. The hides leaving the suspenders were suspended at once in the first retanning liquor at 10° Bé and 33°C for 6 days. The liquor was made up with 50 per cent specially manufactured chestnut extract and 50 per cent ordinary chestnut extract. The hides were then piled for 24 hours, left in water for 4 hours and then entered into the second retannage, carried out in the drum with 300 per cent liquor at 14° Bé and 35°C. for 3 hours.

The experiments carried out with 15,456 kilos of fresh market hides, gave 9,965 kilos of finished leather, equivalent to a yield of 54.5 per cent on raw weight (whole hides). The consumption of tannin was 396 g. of 100 per cent tannin per kilo of raw hide. The leather obtained was firm, full, and of excellent composition. The paper includes tables and graphs illustrating the work carried out and the results obtained. The work shows that it is possible to obtain excellent sole leather by the use of chestnut extract alone using a suitable rapid tanning process. H. C.

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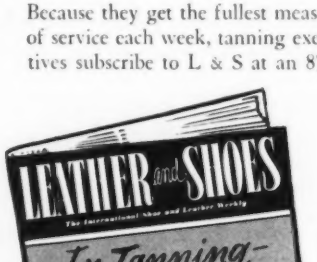

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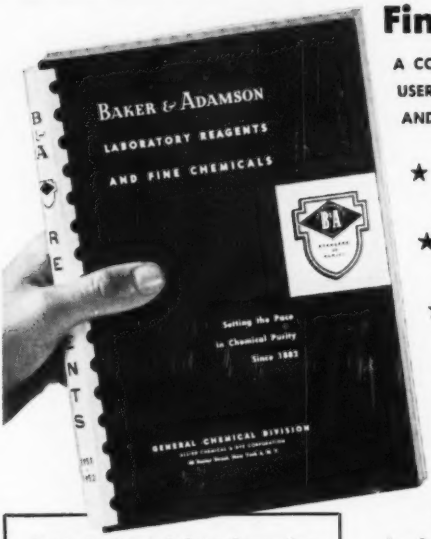

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